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It is perfectly true, as the philosophers say, that life must be understood backwards. But they forget the other proposition, that it must be lived forwards. And if one thinks over that proposition it becomes more and more evident that life can never be understood in time simply because at no particular moment can one find the necessary resting place from which to understand it -backwards.

-Kierkegaard, Journals, 1843

THE UNIVERSITY OF ALBERTA

THE DIFFERENTIAL EQUATIONS OF THE
ONE-ELECTRON TWO-CENTER PROBLEM

by



PETER SENN

A THESIS

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The undersigned certify that they have read, and
recommended to the Faculty of Graduate Studies and
Research, for acceptance, a thesis entitled

The Differential Equations
of the One-Electron Two-
Center Problem

submitted by

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in partial fulfilment of the requirements for
the degree of Master of Science

ABSTRACT

This work is concerned with the general problem of a charged particle in a potential field of two Coulomb centers.

It is common knowledge that the Schroedinger equation for such a system within the Born-Oppenheimer approximation can be separated into a system of three simultaneous second order linear differential equations, if use is made of spheroidal coordinates. This separation of variables gives rise to three separation constants. Since the wave function has to be single valued one of these three constants is required to be integer. For an acceptable solution of the system the remaining two separation constants have to be equal. Furthermore they have to be eigenvalues of a pair of linear differential equations such that their solutions, commonly referred to as "generalized spheroidal wave functions", exist and remain bounded in the physically meaningful intervals of the corresponding variables.

This thesis is divided into five chapters which concentrate on the following topics : (I) Review of existing algorithms for the numerical solution of the system of simultaneous linear differential equations,

originating mainly from Hylleraas and Jaffé. It was found that the radial expansion proposed by Jaffé provides no improvement over the previous Hylleraas expansion in respect to convergence properties if an equal number of terms is considered in both cases.

(II) New expansions are proposed. An angular expansion in ultraspherical polynomials seems sufficiently rapidly convergent for most practical purposes. In addition an angular expansion in confluent hypergeometric functions was found which could possibly be useful if a calculation for a heteronuclear species with large internuclear distance is to be done. For the radial expansion no improvement of the convergence rate could be achieved.

(III) Integral transform techniques are explored. The Laplace transform provides a reasonable explanation for the equivalence of the convergence rates of the two existing radial expansions, but no cure for convergence problems with the radial expansions could be found with the help of integral transforms.

(IV) The system consisting of a particle in the dipole field of two oppositely charged point charges serves as testing ground for the algorithms available up to that point. The need for further improvement of the radial expansions is made apparent. The binding energy of a particle in a dipole field becomes zero at some critical

internuclear distances depending on the state considered. A theorem is formulated stating that these critical distances depend on the angular quantizations exclusively and it furthermore allows us to calculate these critical distances by a simple algorithm consisting essentially of a root search. Numerical values for ten critical internuclear distances are provided in the text. The critical distance for the ground state published previously by Turner and Fox is in agreement with the one calculated by using the present approach.

(V) A radial expansion with the convergence rate accelerating as the "united atom" limit is approached is found.

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CHAPTER I

Introduction and Summary of Previous Work

The theoretical investigation of the hydrogen molecule ion and related species is a problem which arises in many contemporary quantum mechanical treatments as a means of testing theories and algorithms at the ab initio level. The Schroedinger equation for the one-particle two-center problem in the Born-Oppenheimer approximation can be separated into a system of three simultaneous linear DE's (differential equations) if use is made of spheroidal coordinates. Two of these three DE's are closely related to the DE of the spheroidal wave functions frequently encountered in potential theory. In the general case these two DE's are called GSW-DE's ("generalized spheroidal wave DE's") a notation widely accepted in literature.

The algorithms for the solution of the system of DE's were developed at the dawn of modern quantum mechanics mainly by Hylleraas and Jaffé. The radial expansions proposed by Hylleraas and Jaffé are in this text referred to as "Hylleraas-" and "Jaffé-expansion".

They will be shown to generate algorithms with identical rates of convergence. This was not known previously.

The actual DE of the spheroidal wave functions occurs if a homonuclear case or a "particle in a dipole field" is treated. A considerable amount of interest is paid to a system consisting of a particle in the field of two charges with equal magnitude and opposite sign i.e. a dipole field of two point charges. The interest in this special case is partially justified by the fact that from the potential curve for one dipole the potential curve for a different dipole corresponding to different magnitude of the point charges is obtained by simply scaling the internuclear distance.

Since the separation of variables for the one-particle two-center problem in spheroidal coordinates is a common topic in introductory quantum chemistry courses, no effort has been made here to show in detail how this system of linear DE's is obtained from the Schroedinger equation in spheroidal coordinates by separation of variables. Instead existing algorithms for the numerical solution of this system of DE's are presented in this chapter. Later we shall explore schemes which promise some improvement over the existing methods. First new

expansion sets and their convergence properties will be examined. Then integral transform techniques will be considered.

Through the treatment of "the particle in a dipole field" the unresolved problems to this point will be made apparent.

A final effort to devise an algorithm which would eliminate these convergence problems is investigated. However at this point the choice of two non-linear parameters resulting in maximum convergence remains unknown, except for the two limiting cases $R \rightarrow 0$ and $R \rightarrow \infty$ where "R" is the internuclear separation.

The Schroedinger Equation and Separation

of Variables

It can be shown that the Schroedinger equation

$$\{-\frac{1}{2}\nabla^2 - (Z_1/r_1) - (Z_2/r_2)\} \Psi(\vec{r}) = E_e(R) \Psi(\vec{r})$$

in Hartree's atomic units [1]
(*)

can be subjected to separation of variables if use is made of confocal elliptic coordinates.

If r_1 and r_2 in [1] denote the distance of the point $P(r_1, r_2, \phi)$ to the foci and ϕ denotes the angle around the major axis of an ellipse containing P , the coordinates of this point can be expressed as

$$\lambda = \frac{1}{2}(r_1 + r_2)/R, \quad \mu = \frac{1}{2}(r_1 - r_2)/R \quad [2]$$

Writing the wave function Ψ in [1] as a product of functions each depending only on one individual variable

$$\Psi(\lambda, \mu, \phi) = L(\lambda) \cdot M(\mu) \cdot \Phi(\phi) \quad [3]$$

the DE in [1] becomes

$$\{ (d/d\lambda) (\lambda^2 - 1) (d/d\lambda) + (d/d\mu) (1 - \mu^2) (d/d\mu) + [(\lambda^2 - 1)^{-1} + (1 - \mu^2)^{-1}] (d^2/d\phi^2) + R(Z_1 + Z_2)\lambda - R(Z_1 - Z_2)\mu - p^2(\lambda^2 - \mu^2) \} \Psi(\lambda, \mu, \phi) = 0$$

where $p^2 = -\frac{1}{2}E_e(R)R^2$ [4]

(*) Hartree's atomic units are used throughout in this text.

The last DE can be separated into a system of three simultaneous second order lin. (linear) DE's

$$[(d^2/d\phi^2)+m^2]\Phi(\phi) = 0 \quad [5]$$

$$[(d/d\lambda)(\lambda^2-1)(d/d\lambda)-m^2(\lambda^2-1)^{-1}+R(Z_1+Z_2)\lambda-p^2\lambda^2-A_1]L(\lambda) = 0 \quad [6]$$

$$[(d/d\mu)(1-\mu^2)(d/d\mu)-m^2(1-\mu^2)^{-1}-R(Z_1-Z_2)\mu+p^2\mu^2+A_2]M(\mu) = 0$$

$$p^2 = -E_e(R)R^2/2 \quad [7]$$

with three separation constants A_1, A_2 and m^2 . For a proper solution we require $A_1=A_2$.

For [5] the solutions are found by inspection

$$\Phi(\phi) = \exp(im\phi)/\sqrt{2\pi} \quad [8]$$

Since the separation constant m in [5] appears only as m^2 we find that for energy states with $m \neq 0$ we will have a twofold degeneracy corresponding to $m=\pm|m|$. For homonucl. (homonuclear) molecule ions where we have $Z_1=Z_2$ the lin. term in μ in [7] vanishes :

$$[(d/d\mu)(1-\mu^2)(d/d\mu)-m^2(1-\mu^2)^{-1}+(p\mu)^2-A_2]M(\mu) = 0 \quad [9]$$

This DE is then invariant with respect to an operation replacing μ by $-\mu$. Hence [9] has a pair of lin. indep. (linearly independent) solutions of which one is even and one is odd.

Furthermore the solutions to [9] do not explicitly depend on the internuclear distance which we write as R .

Extensive tables for solutions of [9] have been published by Stratton et al. ^(1,2)

Solution of the μ -Equation

Restricting ourselves to the treatment of the homonuclear case, according to E. A. Hylleraas⁽³⁾ the eigenfunctions of [9] can be expanded in associated Legendre polynomials satisfying the following DE :

$$[(d/d\mu)(1-\mu^2)(d/d\mu) + \ell(\ell+1) - m^2(1-\mu^2)^{-1}]P_{\ell}^m(\mu) = 0 \quad [10]$$

For the eigenfunctions of [9] we write the expansion,

$$M(\underline{\ell}, m; \mu) = \sum_{\ell} c_{\ell} P_{\ell}^m(\mu) \quad [11]$$

The summation in [11] ranges from m to ∞ if M and Φ are to have the same parity and the summation index ranges from $(m+1)$ to ∞ if the parities of M and Φ differ. Furthermore this summation index runs only over even integers for bonding states and exclusively over odd integers for antibonding states. The symbol $\underline{\ell}$ in [11] is commonly called an "angular quantum number" or " μ -quantum number" and the expansion in [11] itself in this report is generally referred to as "angular expansion".

Eliminating in [9] the part which is satisfied by the associated Legendre polynomials we can write,

$$\sum_{\ell} c_{\ell} [P_{\mu}^2 + A_2 - \ell(\ell+1)] P_{\ell}^m(\mu) = 0 \quad [12]$$

For the associated Legendre polynomials the following recurrence relation holds,

$$\mu^2 P_{\ell}^m(\mu) = [[(\ell+1-m)(\ell+2-m)]] / [(2\ell+1)(2\ell+3)] P_{\ell+2}^m(\mu)$$

$$\begin{aligned}
& + [[(\ell+1-m) (\ell+1+m)] / [(2\ell+1) (2\ell+3)]] P_{\ell}^m(\mu) \\
& + [[(\ell+m) (\ell-1+m)] / [(2\ell+1) (2\ell-1)]] P_{\ell-2}^m(\mu)
\end{aligned} \tag{13}$$

Due to the separability of variables the nodes of the wave functions have simple geometrical shapes. For the homonuclear case the nodes corresponding to the case $M(\mu)=0$ are two-sheeted hyperboloids with two sheets coinciding in the plane perpendicular through the center of the internuclear axis for the antibonding states.

Substituting the recurrence relation for the generalized Legendre polynomials shown in [13] into [12] the expansion in [11] is defined by the following three-term recurrence relation among the expansion coefficients :

$$\begin{aligned}
& [[(\ell-1-m) (\ell-m)] / [(2\ell-3) (2\ell-1)]] c_{\ell-2} \\
& + [[(A_2 - \ell (\ell+1))] p^{-2} + [(\ell+1-m) (\ell+1+m)] / [(2\ell+3) (2\ell+1)] \\
& + [[(\ell-m) (\ell+m)] / [(2\ell+1) (2\ell-1)]] c_{\ell} \\
& + [[(\ell+2+m) (\ell+1+m)] / [(2\ell+5) (2\ell+3)]] c_{\ell+2} = 0
\end{aligned} \tag{14}$$

This represents an infinite system of lin. homogeneous equations which have a non-trivial solution only if its determinant vanishes. This determinant does vanish for appropriate choices of the separation constant A_2 , i.e. if A_2 in [14] represents the eigenvalues of the corresponding tridiagonal matrix. For similar expressions in the following sections this role of the separation constant will be assumed to be stated implicitly writing an expression of the type [14].

Since $M(\mu)$ represents an expansion with infinitely many terms a crucial question at this point is whether this series converges sufficiently fast for practical purposes.

Hylleraas, who proposed this expansion, using a power series expansion for the separation constant showed that for internucl. (internuclear) distances of chemical interest the rate of convergence is very rapid. (3)

From the recurrence relation [14], it is readily apparent that, for small internucl. distances, $R \approx 0$ the eigenvalue spectrum of the separation constant is

$$A_2(\ell) \approx \ell(\ell+1) \quad \ell = 0, 1, 2, \dots \quad [15]$$

and since for $R \approx 0$ we are approaching a hydrogenlike united atom we have a rough estimate for the electronic energy at hand

$$E_n(R) \approx -(Z_1 + Z_2)^2 / (2n^2) \\ n = 1, 2, 3, \dots \quad (\text{in Hartree's} \\ \text{atomic units}) \quad [16]$$

This limiting behaviour of the electronic energy and the separation constant is of interest in respect to the application of the computer program and will be referred to later.

Qualitative Inspection of the Rate of Convergence for the μ -Expansion

Considering equation [10] which is the DE satisfied by the generalized Legendre polynomials and comparing it with [9] where we have in addition the term " $p^2\mu^2$ " we find that the rate of convergence will be slow if this term becomes dominant. Recalling that,

$$p^2 = -E_e(R)R^2/2 \quad [17]$$

the rate of convergence is expected to be slow for large internuclear distances. The expansion set constitutes the set of eigenfunctions to [9] for the limiting case $R=0$.

For $R \neq 0$ the rate of convergence for large m quantum numbers is expected to be superior to the rate of convergence for small m 's. This trend is predicted because for large m 's the term " $m^2/(1-\mu^2)$ " which is satisfied by all terms in the expansion, constitutes a more significant term of [9] than if m is small, and it is absent altogether if $m=0$.

This argument, although of strictly intuitive nature, was found to hold when it was subjected to tests in numerical calculations.

The Radial Expansions

(A) The Hylleraas Expansion

We recall the DE for the radial wave functions

$$[(\lambda^2-1)(d^2/d\lambda^2)+2\lambda(d/d\lambda)-(m^2/(\lambda^2-1))+2Q\lambda-p^2\lambda^2-A_1]L(\lambda) = 0$$

$$Q = R(Z_1+Z_2)/2 \quad [18] \quad (*)$$

The asymptotic form of $L(\lambda)$ for large λ is easily found. Dividing [18] by λ^2 :

$$[(1-(1/\lambda^2))(d^2/d\lambda^2)-(2/\lambda)(d/d\lambda)-(m^2/(\lambda^2(\lambda^2-1)))+(2Q/\lambda)-p^2-(A_1/\lambda^2)]L(\lambda) = 0 \quad [19]$$

Then for large λ 's the terms with negative powers of λ can be disregarded. This gives us

$$[(d^2/d\lambda^2)-p^2]L(\lambda) \sim 0 \quad [20]$$

which is a second order lin. DE having the char. (characteristic) polynomial

$$r^2-p^2 = 0 \quad [21]$$

and therefore the homogeneous solution to [20] can be written as

$$L(\lambda) \sim c_1 \exp(-p\lambda) + c_2 \exp(p\lambda) \quad [22]$$

If we take $p>0$ the second term in [22] does not contribute to the physically meaningful form of the asymptotic form of L , i.e. $c_2=0$.

(*) This substitution holds throughout and for the symbol " Q_r " used later we have $Q_r \equiv Q$.

When attempting to solve [18] we first investigate suitable transformations to remove bothersome terms.

The first such transformation is

$$L(\lambda) = (\lambda^2 - 1)^{(m/2)} y(\lambda) , \quad [23]$$

removing the term " $m^2/(\lambda^2 - 1)$ " :

$$\begin{aligned} & [(\lambda^2 - 1)(d^2/d\lambda^2) + 2(m+1)\lambda(d/d\lambda) - ((p\lambda)^2 \\ & - 2Q\lambda + A_1 - m(m+1))] y(\lambda) = 0 \end{aligned} \quad [24]$$

Changing the variable

$$\lambda = 1 + (x/2p) , \quad \lambda \in [1, \infty) , \quad x \in [0, \infty) \quad [25]$$

[24] transforms to

$$\begin{aligned} & \{x(x+4p)(d^2/dx^2) + 2[(m+1)(x+2p)](d/dx) + [-(x/2)^2 \\ & + ((Q/p) - p)x + 2Q - p^2 + m(m+1) - A_1]\} y(x) = 0 \end{aligned} \quad [26]$$

For $R=0$ we have

$$p=0 , \quad E_n = -(Z_1 + Z_2)^2 / (2n^2) \text{ and hence } (Q/p) = n \quad [27]$$

Substituting these limiting values for $R=0$ into [26] one obtains the DE

$$\begin{aligned} & \{x^2(d^2/dx^2) + 2(m+1)x(d/dx) + (-(x/2)^2 + nx \\ & - \ell(\ell+1) + m(m+1))\} y(x) = 0 \end{aligned} \quad [28]$$

which has a solution

$$F^0(n, \ell, m; x) = x^{(\ell-m)} \exp(-x/2) L_{n+\ell}^{2\ell+1}(x) \quad [29]$$

where L is an associated Laguerre polynomial.

Hylleraas expands the eigenfunctions of [18] in terms of functions corresponding to the limiting case

$$x \rightarrow 0, R \rightarrow \infty \text{ and equivalently } p \rightarrow \infty,$$

defined by the generating function :

$$\sum_{n=m+1}^{\infty} f(n,m;x) t^{(n-m-1)} = (1-t)^{-(m+1)} \exp(-(x/2)((1+t)/(1-t))) \quad [30]$$

which are solutions of the DE

$$\{x(d^2/dx^2) + (m+1)(d/dx) + (-x/4) + n - ((m+1)/2)\} f(x) = 0 \quad [31]$$

Then using the expansion

$$y(x) = \sum_{n=m+1}^{\infty} c_n f(n-1,m;x) \quad [32]$$

and substituting it into the DE [26]

$$\sum_{n=m+1}^{\infty} c_n \{[(m+1)x(d/dx)] + [(Q/p) - n + ((m+1)/2)]x + [2Q - p^2 - A_1 + m(m+1) - 4p(n - ((m+1)/2))]\} f(n,m;x) = 0 \quad [33]$$

we obtain the above first order lin. DE. The second derivatives were eliminated making use of the diff. (differential) operator satisfied by the expansion functions.

It can be shown that for the expansion terms the following holds :

$$xf(n,m;x) = (2n-m-1)f(n,m;x) - (n-m)f(n+1,m;x) - (n-1)f(n-1,m;x) \quad [34]$$

$$x(d/dx)f(n,m;x) = -((m+1)/2)f(n,m;x) \\ + ((n-m)/2)f(n+1,m;x) - ((n-1)/2)f(n-1,m;x) \quad [35]$$

Substitution for these in [33] leads to,

$$\sum_{n=m+1}^{\infty} c_n \{ f(n-1,m;x) [-(n-1)((Q/p)-n+m+1)] \\ + f(n,m;x) [(2n-m-1)((Q/p)-n)+2Q-p^2-A_1 \\ + (n-1)(m+1)-2p(2n-m-1)] \\ + f(n+1,m;x) [-(n-m)((Q/p)-n)] \} = 0 \quad [36]$$

Then collecting terms with identical $f(n,m;x)$ [36] is obtained in the form,

$$\sum_{n=m+1}^{\infty} \{ [-(n-m-1)((Q/p)-n+1)] c_{n-1} + [(2n-m-1)((Q/p)-n) \\ + 2Q-p^2-A_1 + (n-1)(m+1)-2p(2n-m-1)] c_n \\ - [n((Q/p)-(n-m))] c_{n+1} \} f(n,m;x) = 0 \quad [37]^*$$

In order for the expansion in [37] to hold we simply demand that all coefficients of the $f(n,m;x)$'s vanish. This requirement leads to a recurrence relation among the expansion coefficients. In our case we arrive at the following three-term recurrence relation:

$$-[(n-m-1)((Q/p)-n+1)]c_{n-1} + [(2n-m-1)((Q/p)-n)+2Q-p^2 \\ -A_1 + (n-1)(m+1)-2p(2n-m-1)]c_n - [n((Q/p)-(n-m))]c_{n+1} = 0 \quad [38]$$

* Hylleraas in his original paper lists this formula too, but unfortunately it is misprinted.

This expression is of the same type as [14] and can again be interpreted as an infinite algebraic eigenvalue problem on grounds of the arguments brought forward there.

Since the tridiagonal matrix corresponding to [38] is not real symmetric (or hermitian for that matter) we are not guaranteed that, for the practicable case of truncated expansions, the eigenvalue spectrum for the separation constants be confined to the domain of real numbers.

That in the limiting case of infinite expansions the separation constants are necessarily real is apparent since [6] is self-adjoint.

Since according to the power series expansion for A given by Hylleraas, for finite R the A 's should be in general non-degenerate, there should be no multiplicity of the roots of the char. polynomial of the determinant to be expected. Therefore homing in on the roots along the real axis should generate approximations to the true eigenvalue spectrum rather efficiently.

Convergence Properties of the Hylleraas

Expansion

Numerically the convergence is found to be best for large m quantum numbers, which of course requires high ℓ quantum numbers. In addition convergence turns out to be better for large internuclear distances than for small ones. This behaviour can be expected since the basis functions defined by the generating function in [30] are eigenfunctions of [26] for the case $R \rightarrow \infty$, contrary to the angular expansion which is accurate or diagonalized for the case $R=0$.

(B) The Jaffé Expansion

If we apply to [6] the transformation,

$$L(\lambda) = (\lambda^2 - 1)^{(m/2)} \exp(-p\lambda) L_1(\lambda) \quad [39]$$

we obtain the DE,

$$\begin{aligned} & \{ (\lambda^2 - 1) (d^2/d\lambda^2) + 2[(m+1)\lambda - p(\lambda^2 - 1)] (d/d\lambda) \\ & + 2p\sigma\lambda + m(m+1) - p^2 - A_1 \} L_1(\lambda) = 0 \end{aligned} \quad [40]$$

where in this section,

$$\sigma = (R/p) ((Z_1 + Z_2)/2) - m - 1 \quad [41]$$

Jaffé applied to this DE the bilinear or Möbius transform,

$$\xi = (\lambda - 1)/(\lambda + 1) \quad [42]$$

which maps the area $\text{Re}(\lambda) \geq 1$ onto the disk with radius $= \frac{1}{2}$ tangent to the imaginary axis at the origin in the complex plane. By this transformation the area around the nuclei is moved to the origin, i.e. the center of expansion and the singular point $\lambda = (-1, 0)$ is moved to the point at infinity in the extended complex plane.

This transforms [40] into

$$\begin{aligned} & \{ \xi (1-\xi)^2 D^2 + [(m+1)(1-\xi) + \xi(1-\xi)(m-1) - 4p\xi] D \\ & + [m(m+1) - p^2 - A_1 + 2p\sigma((1+\xi)/(1-\xi))] \} L_1(\xi) = 0 \end{aligned} \quad [43]$$

The last term in [43], which becomes singular at $\xi=1$, can be removed by the substitution

$$L_1(\xi) = 4(1-\xi)^{-\sigma} L_2(\xi) \quad [44]$$

which transforms [43] into :

$$\begin{aligned} & \{ \xi (1-\xi)^2 D^2 + [\xi^2 (1-m-2\sigma) + 2\xi(\sigma-2p-1) + (m+1)] D \\ & + \sigma(\sigma+m)\xi + (\sigma+m)(m+1) + 2p\sigma - p^2 - A_1 \} L_2(\xi) = 0 \end{aligned} \quad [45]$$

Now if we assume for L_2 a power series expansion

$$L_2(\xi) = \sum_n q_n \xi^n \quad [46]$$

using standard procedures we obtain the following three-term recurrence relation among the expansion coefficients in [46] :

$$q_{n-1} [(n-1-\sigma)(n-m-1-\sigma)] + q_n [2n(\sigma-2p-n) + (\sigma+m)(m+1)]$$

$$+2p\sigma - p^2 - A_1] + q_{n+1}[(n+1)(n+m+1)] = 0$$

$$n = 0, 1, 2, 3, \dots \quad [47]$$

It was implied by Jaffé⁽⁵⁾, that his expansion

$$L(\lambda) = (\lambda^2 - 1)^{(m/2)} (\lambda + 1)^\sigma \exp(-p\lambda) \sum_{n=0}^{\infty} q_n ((\lambda - 1)/(\lambda + 1))^n$$

[48]

converges faster than the one found previously by E. A. Hylleraas^{(3), (5)}. However, we can show that the eigenvalues of finite matrices of equal size generated by truncation of the infinite set of lin. (linear) equations of either [38] or [47] are identical.

In other words, considering an equal number of terms in [38] or [47] generates identical finite eigenvalue spectra in both cases. Having an equal number of terms generates in both cases a quantitatively equal degree of approximation to the exact infinite eigenvalue spectrum of the separation constant of the radial expansion.

Proof :

We wish to evaluate the roots of the char. polynomial corresponding to the finite algebraic eigenvalue problem $\det(\tilde{B} - A\tilde{I}) = 0$. In our case $\tilde{B}$ is a tridiagonal n -dimensional matrix with

$$b_{i,i} = \alpha_i, \quad b_{i,i+1} = \beta_{i+1},$$

$$b_{i+1,i} = \gamma_{i+1}$$

[49]

The elements of $\tilde{B}$ would be the coefficients in the systems of lin. equations of [38] or [47] respectively, excluding the separation constant A in the diag.(diagonal) terms. Then the char. polynomial

$$p_n(A) = \det(\tilde{B} - A\tilde{I}) \quad [50]$$

where $\tilde{I}$ is the n -dimensional unit matrix, may be evaluated as follows :

Let $p_k(A)$ denote the leading principal minors of $(\tilde{B} - A\tilde{I})$ of order k . Then expanding $p_k(A)$ by its last row, we have

$$\begin{aligned} p_k(A) &= (\alpha_k - A)p_{k-1}(A) - \beta_k \gamma_k p_{k-2}(A) \\ &\text{with } k = 2, 3, 4, \dots, n \\ &\text{and initially, } p_0(A) = 1, \quad p_1(A) = \alpha_1 - A \end{aligned} \quad [51]$$

This means that the char. polynomial $p_n(A)$ depends only on the diag.(diagonal) elements and the binary products of symmetrically positioned pairs of off-diag.(off-diagonal) elements.

One can readily see, that in [38] and [47] the diag. elements are equal, if it is kept in mind that the expansion index in the Hylleraas expansion begins with $n=m+1$ whereas for the Jaffé expansion it starts at $n=0$. In addition, keeping the difference of the expansion indices in [38] and [47] in mind, it can readily be shown that the binary products of off-diag. elements in [51] are equal using either

the matrix $\tilde{B}$ generated by [37] or [48].

Hence according to what was said previously about the evaluation of the char. polynomial of tridiag.(tridiagonal) matrices, the char. polynomials have to be identical in both cases and of course they will have the same set of roots. This means that the finite eigenvalue spectra for the separation constant are identical in the case of either a truncated Hylleraas or Jaffé expansion as long as an equal number of terms is considered in both cases.

..... end of proof # (*)

The Jaffé expansion was used in almost all the many calculations of this type to date. However it was just shown that it provides no improvement in respect to convergence properties over the previous Hylleraas expansion. The major advantage of the Jaffé expansion probably lies in the fact that the physically meaningful domain of the expansion is a finite interval, making it easier to handle when the wave function is to be used to extract quantum mechanical properties of the system using numerical integration techniques.

(*) Using Laplace transform techniques it can be shown that a functional relationship exists between the Jaffé and the Hylleraas expansion.

CHAPTER II

In this chapter expansions not previously known are presented. It is believed that the one-particle two-center problem is most efficiently treated making use of the theory of special functions. The theory of the generalized hypergeom. (hypergeometric) series and its degenerate cases is used extensively in this chapter.

We often do not know in advance whether the radial or the angular solutions of the GSW-DE are generated by a proposed expansion. Often expressions like "radial expansion" or "angular eigenvalue spectrum" etc. are used in this text. These refer to the type of eigenfunctions and eigenvalue spectra generated by the corresponding expansion. For an expansion to be an angular expansion the wave function must remain bounded in the range $|\mu| \leq 1$ and for the radial expansions the wave functions have to remain bounded for $\lambda \geq 1$. For the angular expansions the homonucl. (homonuclear) case is treated separately.

Expansion of the Angular Generalized Spheroidal
Wave Functions in Ultraspherical Polynomials

The angular GSW-functions are power series expandable solutions of the μ -equation. If we use a power series expansion for these functions the homonuclear case can be treated separately.

If we apply in [7] the transform

$$M(\mu) = (1-\mu^2)^{(m/2)} M_1(\mu) \quad [52]$$

the following DE is obtained

$$\{ (\mu^2-1) (d^2/d\mu^2) + 2(m+1)\mu (d/d\mu) - p^2\mu^2 + R\mu(Z_1-Z_2) + m(m+1) - A_2 \} M_1(\mu) = 0 \quad [53]$$

If $Z_1=Z_2$ a power series expansion of M_1

$$M_1(\mu) = \sum_n q_n \mu^n \quad [54]$$

generates the following three-term recurrence relation among its expansion coefficients

$$-q_{n-2}[p^2] + q_n[n(n-1) + (2n+m)(m+1) - A_2]$$

$$-q_{n+2}[(n+1)(n+2)] = 0$$

$$n = 0, 2, 4, 6, \dots \quad \text{for bonding states}$$

$$n = 1, 3, 5, 7, \dots \quad \text{for antibonding states} \quad [55]$$

For $Z_1 \neq Z_2$ the transformation

$$M_1(\mu) = \exp(-p\mu)M_2(\mu) \quad [56]$$

yields the DE

$$\{(\mu^2-1)D^2+2[(m+1)\mu-p(\mu^2-1)]D+[R(Z_1-Z_2)-2p(m+1)]\mu \\ +m(m+1)-p^2-A_2\} M_2(\mu) = 0 \quad [57]$$

A Taylor series expansion for M_2

$$M_2(\mu) = \sum_n q_n (1-\mu)^n \quad [58]$$

is defined by the three-term recurrence relation

among its expansion coefficients :

$$q_{n+1}[2(n+1)(n+m+1)] + q_n[n(n-1)+2n(m+1-2p)+2p\sigma+m(m+1) \\ -p^2-A_2] = q_{n-1}[2p(n-1-\sigma)] \quad , \quad \sigma = [(R(Z_1-Z_2))/(2p)] - (m+1) \quad [59]$$

For the homonuclear case this expansion can be used as well. However we are going to show that rapidly convergent orthogonal polynomial expansions can be found for the angular eigenfunctions leaving little practical importance to the power series expansions in [54] and [58].

A. The Homonuclear Case

The expansion in associated Legendre polynomials found by Hylleraas⁽³⁾ is very rapidly convergent.

For an expansion in ultraspherical or Gegenbauer polynomials this is the case as well. How the Legendre and the Gegenbauer expansions compare in their rate of convergence for different states and internucl. separation was never systematically investigated by the author. The reason why a new expansion for the homonuclear case will be presented here is because using this type of expansion, we find that we can proceed rather easily to the treatment of the heteronuclear case, for which no expansion has ever been published with a comparable rate of convergence and ease of handling.

The GSW-function to be expanded for the homonucl. case is M_1 satisfying the DE [53].

We try an expansion,

$$M_1(\mu) = \sum_{\ell} q_{\ell} C_{\ell}^{(\alpha)}(\mu) \quad [60]$$

where the $C_{\ell}^{(\alpha)}$ are ultraspherical or Gegenbauer polynomials. Indicating the diff. operator satisfied by these we get our notation straight :

$$\underset{D=d/d\mu}{\mathcal{L}} C_{\ell}^{(\alpha)}(\mu) = \{(\mu^2-1)D^2 + (2\alpha+1)D - \ell(\ell+2\alpha)\} C_{\ell}^{(\alpha)}(\mu) = 0 \quad [61]$$

[61] is a hypergeom. DE with three regular singularities.

In the process of setting up the expansion we will make a choice for the parameter α such that a bothersome term will disappear.

The ultraspherical polynomials satisfy the recurrence relation,

$$\mu C_{\ell}^{(\alpha)}(\mu) = [(\ell+1)C_{\ell+1}^{(\alpha)}(\mu) + (\ell+2\alpha-1)C_{\ell-1}^{(\alpha)}(\mu)] / [2(\ell+\alpha)] \quad [62]$$

from which we derive the desired property,

$$\begin{aligned} \mu^2 C_{\ell}^{(\alpha)}(\mu) &= \{ [(\ell+1)(\ell+2)/(\ell+\alpha+1)] C_{\ell+2}^{(\alpha)}(\mu) \\ &+ [[(\ell+1)(\ell+2\alpha)/(\ell+\alpha+1)] + [\ell(\ell+2\alpha-1)/(\ell+\alpha-1)]] C_{\ell}^{(\alpha)}(\mu) \\ &+ [(\ell+2\alpha-1)(\ell+2(\alpha-1))/(\ell+\alpha-1)] C_{\ell-2}^{(\alpha)}(\mu) \} / [4(\ell+\alpha)] \quad [63] \end{aligned}$$

Now we set up the expansion,

$$\sum_{\ell} q_{\ell} \{ [2m-2\alpha+1] \mu D - p^2 \mu^2 + m(m+1) + \ell(\ell+2\alpha) - A_2 \} C_{\ell}^{(\alpha)}(\mu) = 0 \quad [64]$$

where use has been made of the diff. operator $\underline{G}_{\ell}$ satisfied by the ultraspherical polynomials. If for the parameter α we make the substitution,

$$\alpha = m + (1/2)$$

the coefficient for the first derivative in [64] vanishes. Making use of the property [63] in [64] one gets an expression :

$$\begin{aligned}
\sum_{\ell} q_{\ell} \{ & [[-p^2 (\ell+1) (\ell+2)] / [4 (\ell+\alpha) (\ell+\alpha+1)]] C_{\ell+2}^{(\alpha)}(\mu) \\
& + [(-p^2 / (4 (\ell+\alpha))) [[(\ell+1) (\ell+2\alpha)] / [\ell+\alpha+1]] \\
& + [[\ell (\ell+2\alpha-1)] / [\ell+\alpha-1]] + m(m+1) + \ell (\ell+2\alpha) - A_2] C_{\ell}^{(\alpha)}(\mu) \\
& + [[-p^2 (\ell+2\alpha-1) (\ell+2(\alpha-1))] / [4 (\ell+\alpha) (\ell+\alpha-1)]] C_{\ell-2}^{(\alpha)}(\mu) \} \\
& = 0 \qquad \qquad \qquad [66]
\end{aligned}$$

Collecting equal polynomials we get from this a three-term recurrence relation for the expansion coefficients in [60],

$$\begin{aligned}
& q_{\ell-2} [[-p^2 \ell (\ell+1)] / [4 (\ell+\alpha-2) (\ell+\alpha-1)]] \\
& + q_{\ell} [[-p^2 / (4 (\ell+\alpha))] [[(\ell+1) (\ell+2\alpha)] / [\ell+\alpha+1]] \\
& + [[\ell (\ell+2\alpha-1)] / [\ell+\alpha-1]] + m(m+1) + \ell (\ell+2\alpha) - A_2] \\
& + q_{\ell+2} [[-p^2 (\ell+2\alpha) (\ell+2\alpha+1)] / [4 (\ell+\alpha+2) (\ell+\alpha+1)]] = 0 \qquad [67]
\end{aligned}$$

with $\ell = 0, 2, 4, 6, \dots$ for bonding states
and $\ell = 1, 3, 5, 7, \dots$ for antibonding states

B. The Heteronuclear case

In the heteronuclear case M_2 , which satisfies the DE [57], can be expanded in ultraspherical polynomials.

In order to shorten the expressions the following substitution will be made :

$$B = R((Z_1 - Z_2)/2) - p(m+1) \quad [68]$$

In addition to the recurrence relation [62] the following differentiation formula is needed :

$$\begin{aligned} (\mu^2 - 1) (d/d\mu) C_{\ell}^{(\alpha)}(\mu) &= \{\ell(\ell+1) C_{\ell+1}^{(\alpha)}(\mu) \\ &- (\ell+2\alpha)(\ell+2\alpha-1) C_{\ell-1}^{(\alpha)}(\mu)\} / [2(\ell+\alpha)] \end{aligned} \quad [69]$$

From [57], making use of the diff. operator $\underline{G}_{\ell}$ satisfied by the ultraspherical polynomials and assuming for M_2 an expansion in ultraspherical polynomials,

$$M_2(\mu) = \sum_{\ell} q_{\ell} C_{\ell}^{(\alpha)}(\mu) \quad [70]$$

one gets an expression,

$$\begin{aligned} \sum_{\ell} q_{\ell} \{ [(2m-2\alpha+1)\mu - 2p(\mu^2-1)] (d/d\mu) + 2B\mu \\ + \ell(\ell+2\alpha) + m(m+1) - p^2 - A_2 \} C_{\ell}^{(\alpha)}(\mu) = 0 \end{aligned} \quad [71]$$

The parameter α is chosen such that the linear term for the first derivative vanishes,

$$2m-2\alpha+1 = 0 \longrightarrow \alpha = m + (1/2) \quad [72]$$

which is the same as used for the homonucl. case.

Substitution for the properties [62] and [69] of the ultraspherical polynomials gives an expression of the same type as [66]. If we collect equal powers in this expression and require their coefficients to vanish we arrive again at a recurrence relation among the expansion coefficients in [70]. It is the following three-term recurrence relation :

$$\begin{aligned}
 & [[\ell(B-(\ell-1)p)]/[\ell+\alpha-1]]q_{\ell-1} \\
 & + [\ell(\ell+2\alpha)+m(m+1)-p^2-A_2]q_{\ell} \\
 & + [[(\ell+2\alpha)(B+(\ell+2\alpha+1)p)]/[\ell+\alpha+1]]q_{\ell+1} = 0
 \end{aligned} \tag{73}$$

where $\ell = 0, 1, 2, 3, \dots$

Examining this recurrence relation we find that for the expansion [70] the corresponding algebraic eigenvalue problem is diagonalized if $R=0$ and $p=0$ i.e. in the "united atom" limit.

From listings in Fig. I it can be seen that taking only 15 expansion terms a reasonable number of significant figures is obtained with this expansion. The eigenvalue referred to in Fig. I is the second lowest eigenvalue of the angular expansions which is listed in Appendix II.

For HeH^{++} the state $|n; \ell, m\rangle \equiv |6; 2, 1\rangle$ was calculated for five hundred internuclear distances from $R=0.2$ to $R=100.0$ with an increment of $\Delta R=0.2$ to 13 significant figures using 40 expansion terms for both the angular and the radial expansion.

The computer program used for this purpose is listed in Appendix I.

Fig. I : The number of significant decimal figures^(*) for the second lowest eigenvalue (Separation constant !)

with $m=0$ of the angular expansion in ultraspherical polynomials using 10(Fig. Ia) and 15(Fig. Ib) expansion terms.

(a)		(**)										
	p^2	0	1	2	3	4	5	6	7	8	9	10
Q_a	0.5	>16	12	9	7	5	5	5	4	4	4	3
	1.5	>16	12	9	7	6	5	4	4	3	3	3
	2.5	>16	13	10	8	6	5	4	3	2	2	2
	3.5	15	13	10	10	7	6	5	4	2	2	2
	4.5	13	14	11	9	7	8	5	3	4	3	3
	5.5	12	13	11	9	7	6	6	6	5	5	4
	6.5	11	13	9	9	8	8	7	6	6	5	5
	7.5	9	13	11	10	9	8	8	7	6	6	5
	8.5	9	13	13	11	9	9	8	7	8	6	6
	9.5	9	12	12	11	10	9	9	8	7	7	8

(*) Double precision was used within a Fortran IV source, which means a mantissa of 14 hexadecimal figures.

(**) $Q_a = \frac{1}{2}R(Z_1 - Z_2)$

(b)

$Q_a \backslash p^2$	0	1	2	3	4	5	6	7	8	9	10
0.5	>16	>16	>16	15	13	13	12	11	11	10	9
1.5	>16	>16	16	16	14	12	11	11	10	10	9
2.5	>16	>16	>16	>16	15	13	11	10	9	9	8
3.5	>16	>16	>16	>16	15	13	12	11	9	8	8
4.5	>16	>16	>16	>16	16	15	12	10	10	10	9
5.5	>16	>16	16	16	15	14	13	13	12	11	10
6.5	15	15	14	>16	16	16	14	13	12	12	12
7.5	15	16	15	>16	>16	16	15	14	13	12	12
8.5	>16	15	>16	>16	>16	16	15	14	15	13	12
9.5	16	>16	>16	>16	>16	>16	16	15	14	14	14

For the angular expansions one can take,

$$(i) \quad p = |p| \quad , \quad R = |R|$$

$$(ii) \quad p = |p| \quad , \quad R = -|R|$$

$$(iii) \quad p = -|p| \quad , \quad R = |R|$$

$$(iv) \quad p = -|p| \quad , \quad R = -|R| \quad [73.5]$$

which essentially corresponds to a change in sign for the variable and replacing p by $-p$ in the transformation [56]. For the expansions in ultraspherical polynomials the rates of convergence in respect to the separation constant are equal in all four cases.

Expansion of the Angular Spheroidal Wave Functions

in Spherical Bessel Functions

It can be shown that for the angular spheroidal wave functions (homonuclear case) an expansion in modified Bessel functions is possible,

$$M_1(\mu) = \sum_n q_n u_n(p\mu) = \sum_n q_n (p\mu)^n K_n(p\mu) \quad [74]$$

$$M_1(\mu) = \sum_n q_n v_n(p\mu) = \sum_n r_n (p\mu)^{-n} K_n(p\mu) \quad [75]$$

where the K_n 's are modified Bessel functions of the third kind and M_1 is defined by [52] and [53].

The linear differential operators satisfied by the expansion functions are,

$$\{xD^2 + (1-2n)D - x\} u_n(x) = 0 \quad [76]$$

$$\{xD^2 + (1+2n)D - x\} v_n(x) = 0 \quad [77]$$

Examining these two operators we can easily see that the u_n 's and v_n 's are either even or odd functions. The properties needed for the expansion are easily derived from the theory of Bessel functions,

$$xDu_n(x) = 2nu_n(x) - u_{n+1}(x) \quad [78]$$

$$D^2u_n(x) = (1-2n)u_{n-1}(x) + u_n(x) \quad [79]$$

$$xDv_n(x) = -2nv_n(x) - v_{n-1}(x) \quad [80]$$

$$D^2v_n(x) = (1+2n)v_{n+1}(x) + v_n(x) \quad [81]$$

Scaling the variable,

$$x = p\mu \quad [82]$$

[53] becomes,

$$\{(x^2 - p^2)D^2 + 2(m+1)x D - x^2 + m(m+1) - A_2\} M_1(x) = 0 \quad [83]$$

Substituting the expansions [74] and [75] into [83] and making use of the linear differential operators [76] and [77] satisfied by the expansion functions one obtains the following expressions :

$$\sum_n q_n \{-p^2 D^2 + [2(m+n)+1]x D + m(m+1) - A_2\} u_n(x) = 0 \quad [84]$$

$$\sum_n r_n \{-p^2 D^2 + [2(m-n)+1]x D + m(m+1) - A_2\} v_n(x) = 0 \quad [85]$$

The differential relations [80] and [81] for the v_n 's can be obtained from the ones for the u_n 's replacing n by $-n$ and the same holds for the differential equations for the u_n 's and v_n 's. Therefore the recurrence relations for the two different expansions will predictably differ again just by the sign of n .

Hence we stop working on the expansion [75].

Substitution of the differential relations [78] and [79] into [84] and applying standard expansion techniques gives rise to the following three-term recurrence relation among the expansion coefficients in [74] :

$$q_{n-1} [1 - 2(n+m)] + q_n [(2n+m)(2n+m+1) - p^2 - A_2] + q_{n+1} [p^2(1+2n)] = 0 \quad [86]$$

The algebraic eigenvalue problem associated with [86] is bisected at $n=\pm\frac{1}{2}$.

If we take

$$|n| = \frac{1}{2}, \frac{3}{2}, \frac{5}{2}, \frac{7}{2}, \frac{9}{2}, \dots \quad \text{and } n \leq -m - \frac{1}{2} \quad [87]$$

$$\text{or } n = \dots, -k, -(k-1), \dots, -1, 0, 1, \dots, (k-1), k, \dots \\ -\infty < k < \infty \quad [88]$$

the eigenvalue spectra for the homonucl. angular expansions are obtained. The expansion with the expansion index as in [87] is more rapidly convergent than the one with the expansion index being an integer number as in [88].

The Bessel functions of integer order can be used for even or odd angular states, whereas for the spherical Bessel functions the following holds :

$$\begin{aligned} n < 0 & \dots \text{ even angular states} \\ n > 0 & \dots \text{ odd angular states} \end{aligned}$$

If we seek an expansion in modified Bessel functions of the first (and second) kind

$$M_1(\mu) = \sum_n q_n(p\mu)^n I_n(p\mu) \quad [89]$$

the following recurrence relation holds for the q_n 's in [89] :

$$\begin{aligned} -p^2 [2n+1] q_{n+1} + [(2n+m+1)(2n+m) - p^2 - A_2] q_n \\ + [2(n+m) - 1] q_{n-1} = 0 \end{aligned} \quad [90]$$

If we choose expansion terms where a negative power of " $p\mu$ " was factored out the resulting change in the

recurrence relation for the corresponding expansion coefficients will only be a change in sign for n .

Considering [90] as a system of linear equations it would differ from the one in [86] only by the sign of the off-diagonal elements. This means that for an equal number of terms considered their eigenvalue spectra will be identical. This can be shown to hold making use of the same arguments used to exhibit the equivalence of the Hylleraas and the Jaffé expansion. The equivalence of [90] and [86] in terms of convergence properties of A_2 however is even more obvious, because we can show, that a pair of equidimensional matrices whose off-diagonal elements have opposite signs but are equal in magnitude, have identical eigenvalues.

Theorem : The two equidimensional matrices $\tilde{B}$ and $\tilde{B}^\circ$ differing from each other only by the signs of all their off-diagonal elements (but not the diagonal elements !) have identical eigenvalue spectra.

Proof : Imagine the determinants of " $\det(\tilde{B} - \tau \tilde{I}) = 0$ " and " $\det(\tilde{B}^\circ - \epsilon \tilde{I}) = 0$ " factored out in $n!$ different permutations of the matrix elements, appropriate to calculate the determinants. Since every one of these permutations contains $n-1$ off-diagonal elements the resulting characteristic polynomials will differ only

by a factor of $(-1)^{(n-1)}$ of all their coefficients. Therefore they will have the same set of roots.

end of proof $\square$

For $R=0$ the eigenvalue problems associated with the modified Bessel function expansions are diagonalized. For example taking [74] the analytic expression for $R=0$ would be :

$$M_1(\ell, m; \mu) = \sum_{n=0}^{n=|\ell-m|} \left\{ \left\{ \prod_{k=0}^{k=n} [A_2 - (k-m)(k-m+1)] / [k-2(m-1)] \right\} (p\mu)^{-(n+(1/2))} K_{n-(1/2)}(p\mu) \right\}$$

[91]

where as mentioned previously the separation constants for $R=0$ are : $A_2 = \ell(\ell+1)$.

Expansions of the Generalized Spherical Wave Functions
in Confluent Hypergeometric Functions

When in the following two sections we refer to the GSW-DE we usually assume it to be in a form where the coefficients are specified as follows :

$$\{[a_1x+a_2x^2]D^2+[b_0+b_1x+b_2x^2]D+[k_0+k_1x]\} Sw(x) = 0 \quad [92]$$

and in general we assume that in [92],

$$|a_2|=|b_2|=1 \quad [93]$$

We are going to show that for any choice of the parameters in [92] an expansion in terms of any solution to the linear differential operator,

$$\underline{L}_k g_k(\alpha, \gamma; x) = \{xD^2+[\gamma-x]D-\alpha\}g_k(\alpha, \gamma; x) = 0 \quad [94]$$

can be found.

The power series expansion of the above DE is

$$\begin{aligned} g_1(\alpha, \gamma; x) &= [\Gamma(\gamma)/\Gamma(\alpha)] \sum_{n=0}^{\infty} \{[\Gamma(\alpha+n)/\Gamma(\gamma+n)] [x^n/n!]\} \\ &= \Phi(\alpha, \gamma; x) \end{aligned} \quad [95]$$

Using the notation of the generalized hypergeometric series,

$$g_1(\alpha, \gamma; x) \equiv {}_1F_1(\alpha, \gamma; x) \quad [96]$$

which we denote by Humbert's symbol $\Phi(\alpha, \gamma; x)$.

The roots of the indicial equation of [94] are 0 and $1-\gamma$.

If we put in [94],

$$g_k(\alpha, \gamma; x) = x^{(1-\gamma)} h_k(\alpha, \gamma; x) \quad [97]$$

we obtain the DE,

$$\{xD^2 + (2-\gamma-x)D + (\gamma-\alpha-1)\} h_k(\alpha, \gamma; x) = 0 \quad [98]$$

which is of the same form as [94] and hence its power series expansion according to the adopted formalism is :

$$h_k(\alpha, \gamma; x) = \phi(\alpha-\gamma+1, 2-\gamma; x) \quad [99]$$

Therefore (for non-integer γ 's) a second linearly independent solution is :

$$g_2(\alpha, \gamma; x) = x^{(1-\gamma)} \phi(\alpha-\gamma+1, 2-\gamma; x) \quad [100]$$

The functions g_1 and g_2 form a fundamental set of solutions of [94], provided that γ is not an integer.

Substituting in [94],

$$g_k(\alpha, \gamma; x) = \exp(x) h_k(\alpha, \gamma; x) \quad [101]$$

it transforms into :

$$\{xD^2 + (\gamma+x)D + (\gamma-\alpha)\} h_k(\alpha, \gamma; x) = 0 \quad [102]$$

Replacing x by $-x$ gives,

$$\{xD^2 + (\gamma-x)D + (\alpha-\gamma)\} h_k(\alpha, \gamma; -x) = 0 \quad [103]$$

which again is of the same type as [94] having the following system of linearly independent solutions :

$$h_1(\alpha, \gamma; -x) = \phi(\gamma-\alpha, \gamma; x) \quad [104]$$

$$h_2(\alpha, \gamma; -x) = x^{(1-\gamma)} \phi(1-\alpha, 2-\gamma; x) \quad [105]$$

Therefore according to the substitution [101] the solutions to [94] can as well be written as

$$g_3(\alpha, \gamma; x) = \exp(x) \Phi(\gamma - \alpha, \gamma; -x) \quad [106]$$

$$g_4(\alpha, \gamma; x) = \exp(x) x^{(1-\gamma)} \Phi(1-\alpha, 2-\gamma; -x) \quad [107]$$

Since [94] can have a fundamental set of only two lin. indep. solutions and considering the limiting behaviour of g_{1-4} at the origin, one comes readily to the conclusion that $g_1 \equiv g_3$ and $g_2 \equiv g_4$.

The relation

$$\Phi(\alpha, \gamma; x) = \exp(x) \Phi(\gamma - \alpha, \gamma; x) \quad [108]$$

is indeed known as Kummer's transformation or Kummer's first formula, which in turn constitutes a limiting case of Euler's transformation of the hypergeom. series.

Frequently the solutions to [94] are expressed in terms of Ψ functions. The Ψ function is readily obtained by seeking an integral representation of a solution to [94] using an appropriate kernel

$$g_5(\alpha, \gamma; x) = \int_{z_0}^{z_1} [\exp(-xt) S(t)] dt \quad [109]$$

where z_0 and z_1 are complex numbers to be properly chosen.

Using standard operations one finds that the kernel S must satisfy

$$\{t(1-t)(d/dt) + [(2-\gamma)t + 1 - \alpha]\} S(t) = 0 \quad [110]$$

and z_0 and z_1 must be chosen such that

$$-\exp(-xt)t(1+t)S(t)\Big|_{z_0}^{z_1} = 0 \quad [111]$$

Since [110] is a first order lin. DE it may readily be integrated.

$$S(t) = t^{(\alpha-1)}(1+t)^{(\gamma-\alpha-1)} \quad [112]$$

We shall assume that $\text{Re}(z) > 0$ and $\text{Re}(\alpha) > 0$. Then [111] will be satisfied for $z_0 \equiv 0$ and $z_1 \rightarrow \infty$. Therefore an integral representation of the type [109] can be written as :

$$\begin{aligned} g_5(\alpha, \gamma; x) &= \Psi(\alpha, \gamma; x) \\ &= \int_0^\infty [\exp(-xt)t^{(\alpha-1)}(1+t)^{(\gamma-\alpha-1)}]dt \end{aligned} \quad [113]$$

We can rotate the path of integration in the complex plane, i.e. $z_1 = \infty$ is not unique. One can write more generally $z_1 = |\infty| \exp(i\phi)$, which extends the domain of definition :

$$\begin{aligned} \Psi(\alpha, \gamma; x) &= [\Gamma(\alpha)]^{-1} \int_0^{|\infty| \exp(i\phi)} [\exp(-xt)t^{(\alpha-1)}(1+t)^{\gamma-\alpha-1}]dt \\ &\text{with } \text{Re}(\alpha) > 0, -\pi < \phi < \pi \text{ and } -\frac{1}{2}\pi < \phi + \arg(x) < \frac{1}{2}\pi. \end{aligned} \quad [114]$$

Of course, according to the transformations [97] and [101] to which the DE of the confluent hypergeom. functions was subjected, one finds a set g_{5-8} corresponding to g_{1-4} found previously :

$$g_5(\alpha, \gamma; x) = \Psi(\alpha, \gamma; x) \quad [115]$$

$$g_6(\alpha, \gamma; x) = x^{(1-\gamma)} \Psi(\alpha-\gamma+1, 2-\gamma; x) \quad [116]$$

$$g_7(\alpha, \gamma; x) = \exp(x) \Psi(\gamma-\alpha, \gamma; -x) \quad [117]$$

$$g_8(\alpha, \gamma; x) = \exp(x) x^{(1-\gamma)} \Psi(1-\alpha, 2-\gamma; -x) \quad [118]$$

At this point we certainly would like to know first of all which ones of g_{5-8} are identical pairs and in addition we wish to find out how the Ψ function relates to the Φ function.

We start with the second part of our quest stating the important relationship,

$$\begin{aligned}\Psi(\alpha, \gamma; x) = & [\Gamma(1-\gamma)/\Gamma(\alpha-\gamma+1)]\Phi(\alpha, \gamma; x) \\ & + [\Gamma(\gamma-1)/\Gamma(\alpha)]x^{(1-\gamma)}\Phi(\alpha-\gamma+1, 2-\gamma; x)\end{aligned}\quad [119]$$

which we borrow from literature. ⁽⁶⁾

A readily apparent consequence of [119] is,

$$\Psi(\alpha, \gamma; x) = x^{(1-\gamma)}\Psi(\alpha-\gamma+1, 2-\gamma; x)\quad [120]$$

i.e. $g_5 \equiv g_6$. Then g_7 and g_8 must be a second linearly dependent pair. We find : $g_8 = -\exp(\text{sgn}(\text{Im}(x))i\gamma\pi)g_7$.

Finally we list all the relationships required for an expansion of Sw in terms of confluent hypergeometric functions. (*)

Eight solutions to the confluent hypergeometric differential operator were presented. Since we can choose either α or γ as the expansion index sixteen different expansions of the Sw 's can potentially be generated :

$$Sw_1(x) = \sum_n q_{1,n} \Phi(n, c_1; x) = \sum_n q_{1,n} g_1(n, c_1; x)\quad [121]$$

$$Sw_2(x) = \sum_n q_{2,n} \Psi(n, c_2; x) = \sum_n q_{2,n} g_2(n, c_2; x)\quad [122]$$

(*) The Sw 's are the eigenfunctions of the GSW-DE in [92]

$$Sw_3(x) = \sum_n q_{3,n} \phi(c_{3,n};x) = \sum_n q_{3,n} g_3(c_{3,n};x) \quad [123]$$

$$Sw_4(x) = \sum_n q_{4,n} \psi(c_{4,n};x) = \sum_n q_{4,n} g_4(c_{4,n};x) \quad [124]$$

$$Sw_5(x) = \sum_n q_{5,n} x^{(c_5-1)} \phi(n, c_5; x) = \sum_n q_{5,n} g_5(n, c_5; x) \quad [125]$$

$$Sw_6(x) = \sum_n q_{6,n} x^{(c_6-1)} \psi(n, c_6; x) = \sum_n q_{6,n} g_6(n, c_6; x) \quad [126]$$

$$Sw_7(x) = \sum_n q_{7,n} x^{(n-1)} \phi(c_7, n; x) = \sum_n q_{7,n} g_7(c_7, n; x) \quad [127]$$

$$Sw_8(x) = \sum_n q_{8,n} x^{(n-1)} \psi(c_8, n; x) = \sum_n q_{8,n} g_8(c_8, n; x) \quad [128]$$

$$Sw_9(x) = \sum_n q_{9,n} e^{-x} \phi(n, c_9; x) = \sum_n q_{9,n} g_9(n, c_9; x) \quad [129]$$

$$Sw_{10}(x) = \sum_n q_{10,n} e^{-x} \psi(n, c_{10}; x) = \sum_n q_{10,n} g_{10}(n, c_{10}; x) \quad [130]$$

$$Sw_{11}(x) = \sum_n q_{11,n} e^{-x} \phi(c_{11}, n; x) = \sum_n q_{11,n} g_{11}(c_{11}, n; x) \quad [131]$$

$$Sw_{12}(x) = \sum_n q_{12,n} e^{-x} \psi(c_{12}, n; x) = \sum_n q_{12,n} g_{12}(c_{12}, n; x) \quad [132]$$

$$\begin{aligned} Sw_{13}(x) &= \sum_n q_{13,n} x^{(c_{13}-1)} e^{-x} \phi(n, c_{13}; x) \\ &= \sum_n q_{13,n} g_{13}(n, c_{13}; x) \end{aligned} \quad [133]$$

$$\begin{aligned} Sw_{14}(x) &= \sum_n q_{14,n} x^{(c_{14}-1)} e^{-x} \psi(n, c_{14}; x) \\ &= \sum_n q_{14,n} g_{14}(n, c_{14}; x) \end{aligned} \quad [134]$$

$$\begin{aligned} Sw_{15}(x) &= \sum_n q_{15,n} x^{(n-1)} e^{-x} \phi(c_{15}, n; x) \\ &= \sum_n q_{15,n} g_{15}(c_{15}, n; x) \end{aligned} \quad [135]$$

$$\begin{aligned} Sw_{16}(x) &= \sum_n q_{16,n} x^{(n-1)} e^{-x} \psi(c_{16}, n; x) \\ &= \sum_n q_{16,n} g_{16}(c_{16}, n; x) \end{aligned} \quad [136]$$

The expansion sets g_{1-16} are eigenfunctions of second order linear differential operators,

$$\underline{L}_k g_k(\alpha, \gamma; x) = 0 \quad [137]$$

The list of these operators for g_{1-16} is given below :

$$\underline{L}_1 \equiv xD^2 + (c_1 - x)D - n \quad [138]$$

$$\underline{L}_2 \equiv xD^2 + (c_2 - x)D - n \quad [139]$$

$$\underline{L}_3 \equiv xD^2 + (n - x)D - c_3 \quad [140]$$

$$\underline{L}_4 \equiv xD^2 + (n - x)D - c_4 \quad [141]$$

$$\underline{L}_5 \equiv xD^2 + (2 - c_5 - x)D + (c_5 - n - 1) \quad [142]$$

$$\underline{L}_6 \equiv xD^2 + (2 - c_6 - x)D + (c_6 - n - 1) \quad [143]$$

$$\underline{L}_7 \equiv xD^2 + (2 - n - x)D + (n - c_7 - 1) \quad [144]$$

$$\underline{L}_8 \equiv xD^2 + (2 - n - x)D + (n - c_8 - 1) \quad [145]$$

$$\underline{L}_9 \equiv xD^2 + (c_9 + x)D + (c_9 - n) \quad [146]$$

$$\underline{L}_{10} \equiv xD^2 + (c_{10} + x)D + (c_{10} - n) \quad [147]$$

$$\underline{L}_{11} \equiv xD^2 + (n + x)D + (n - c_{11}) \quad [148]$$

$$\underline{L}_{12} \equiv xD^2 + (n + x)D + (n - c_{12}) \quad [149]$$

$$\underline{L}_{13} \equiv xD^2 + (2 - c_{13} + x)D + (1 - n) \quad [150]$$

$$\underline{L}_{14} \equiv xD^2 + (2 - c_{14} + x)D + (1 - n) \quad [151]$$

$$\underline{L}_{15} \equiv xD^2 + (2 - n + x)D + (1 - c_{15}) \quad [152]$$

$$\underline{L}_{16} \equiv xD^2 + (2 - n + x)D + (1 - c_{16}) \quad [153]$$

Now we list the three-term recurrence relations for

the different expansion sets :

$$(c_1-n)g_1(n-1, c_1; x) + (2n-c_1+x)g_1(n, c_1; x) - ng_1(n+1, c_1; x) = 0 \quad [154]$$

$$g_2(n-1, c_2; x) - (2n-c_2+x)g_2(n, c_2; x) + n(n-c_2+1)g_2(n+1, c_2; x) = 0 \quad [155]$$

$$n(n-1)g_3(c_3, n-1; x) - n(n-1+x)g_3(c_3, n; x) + (n-c_3)xg_3(c_3, n+1; x) = 0 \quad [156]$$

$$(n-c_4-1)g_4(c_4, n-1; x) - (n-1+x)g_4(c_4, n; x) + xg_4(c_4, n+1; x) = 0 \quad [157]$$

$$(c_5-n)g_5(n-1, c_5; x) + (2n-c_5+x)g_5(n, c_5; x) - ng_5(n+1, c_5; x) = 0 \quad [158]$$

$$g_6(n-1, c_6; x) - (2n-c_6+x)g_6(n, c_6; x) + n(n-c_6+1)g_6(n+1, c_6; x) = 0 \quad [159]$$

$$n(n-1)xg_7(c_7, n-1; x) - n(n-1+x)g_7(c_7, n; x) + (n-c_7)g_7(c_7, n+1; x) = 0 \quad [160]$$

$$(n-c_8-1)xg_8(c_8, n-1; x) - (n-1+x)g_8(c_8, n; x) + g_8(c_8, n+1; x) = 0 \quad [161]$$

$$(c_9-n)g_9(n-1, c_9; x) + (2n-c_9+x)g_9(n, c_9; x) - ng_9(n+1, c_9; x) = 0 \quad [162]$$

$$g_{10}(n-1, c_{10}; x) - (2n-c_{10}+x)g_{10}(n, c_{10}; x) + n(n-c_{10}+1)g_{10}(n+1, c_{10}; x) = 0 \quad [163]$$

$$n(n-1)g_{11}(c_{11}, n-1; x) - n(n-1+x)g_{11}(c_{11}, n; x) + (n-c_{11})xg_{11}(c_{11}, n+1; x) = 0 \quad [164]$$

$$(n-c_{12}-1)g_{12}(c_{12},n-1;x)-(n-1+x)g_{12}(c_{12},n;x) \\ +xg_{12}(c_{12},n+1;x) = 0 \quad [165]$$

$$(c_{13}-n)g_{13}(n-1,c_{13};x)+(2n-c_{13}+x)g_{13}(n,c_{13};x) \\ -ng_{13}(n+1,c_{13};x) = 0 \quad [166]$$

$$g_{14}(n-1,c_{14};x)-(2n-c_{14}+x)g_{14}(n,c_{14};x) \\ +n(n-c_{14}+1)g_{14}(n+1,c_{14};x) = 0 \quad [167]$$

$$n(n-1)xg_{15}(c_{15},n-1;x)-n(n-1+x)g_{15}(c_{15},n;x) \\ +(n-c_{15})g_{15}(c_{15},n+1;x) = 0 \quad [168]$$

$$(n-c_{15}-1)xg_{16}(c_{16},n-1;x)-(n-1+x)g_{16}(c_{16},n;x) \\ +g_{16}(c_{16},n+1;x) = 0 \quad [169]$$

These three-term recurrence relations can be derived from Gauss' relations between contiguous functions.

The differential relations listed below are readily derived from the theory of Gauss' hypergeometric series as well. Having these we will have everything required for the expansions at our disposal.

$$xDg_1(n,c_1;x) = n[g_1(n+1,c_1;x)-g_1(n,c_1;x)] \quad [170]$$

$$xDg_2(n,c_2;x) = n[(n-c_2+1)g_2(n+1,c_2;x)-g_2(n,c_2;x)] \\ = (n-c_2+x)g_2(n,c_2;x)-g_2(n-1,c_2;x) \quad [171]$$

$$Dg_3(c_3,n;x) = [(c_3/n)-1]g_3(c_3,n+1;x)+g_3(c_3,n;x) \\ = (1-n)[g_3(c_3,n;x)-g_3(c_3,n-1;x)]/x \quad [172]$$

$$Dg_4(c_4,n;x) = -g_4(c_4,n+1;x)+g_4(c_4,n;x) \quad [173]$$

$$xDg_5(n,c_5;x) = ng_5(n+1,c_5;x)+(c_5-n-1)g_5(n,c_5;x) \quad [174]$$

$$\begin{aligned}
 xDg_6(n, c_6; x) &= n(n - c_6 + 1)g_6(n+1, c_6; x) + (c_6 - n - 1)g_6(n, c_6; x) \\
 &= (n - 1 + x)g_6(n, c_6; x) - g_6(n - 1, c_6; x) \quad [175]
 \end{aligned}$$

$$\begin{aligned}
 Dg_7(c_7, n; x) &= [(c_7/n) - 1]g_7(c_7, n+1; x) + (n - 1 + x)g_7(c_7, n; x) / x \\
 &= (n - 1)g_7(c_7, n - 1; x) \quad [176]
 \end{aligned}$$

$$xDg_8(c_8, n; x) = -g_8(c_8, n+1; x) + (n - 1 + x)g_8(c_8, n; x) \quad [177]$$

$$xDg_9(n, c_9; x) = ng_9(n+1, c_9; x) - (n + x)g_9(n, c_9; x) \quad [178]$$

$$\begin{aligned}
 xDg_{10}(n, c_{10}; x) &= n(n - c_{10} + 1)g_{10}(n+1, c_{10}; x) - \\
 (n + x)g_{10}(n, c_{10}; x) &= (n - c_{10})g_{10}(n, c_{10}; x) \\
 - g_{10}(n - 1, c_{10}; x) &\quad [179]
 \end{aligned}$$

$$\begin{aligned}
 Dg_{11}(c_{11}, n; x) &= [(c_{11}/n) - 1]g_{11}(c_{11}, n+1; x) \\
 &= [(1 - n - x)g_{11}(c_{11}, n; x) + (n - 1)g_{11}(c_{11}, n - 1; x)] \\
 &\quad / x \quad [180]
 \end{aligned}$$

$$Dg_{12}(c_{12}, n; x) = -g_{12}(c_{12}, n+1; x) \quad [181]$$

$$xDg_{13}(n, c_{13}; x) = ng_{13}(n+1, c_{13}; x) + (c_{13} - n - 1 - x)g_{13}(n, c_{13}; x) \quad [182]$$

$$\begin{aligned}
 xDg_{14}(n, c_{14}; x) &= n(n - c_{14} + 1)g_{14}(n+1, c_{14}; x) + (c_{14} - n - 1 - x) \\
 g_{14}(n, c_{14}; x) &= (n - 1)g_{14}(n, c_{14}; x) - g_{14}(n - 1, c_{14}; x) \quad [183]
 \end{aligned}$$

$$\begin{aligned}
 Dg_{15}(c_{15}, n; x) &= [(c_{15}/n) - 1]g_{15}(c_{15}, n+1; x) \\
 + (n - 1)g_{15}(c_{15}, n; x) &= -g_{15}(c_{15}, n; x) + (n - 1)g_{15}(c_{15}, n - 1; x) \\
 &\quad [184]
 \end{aligned}$$

$$xDg_{16}(c_{16}, n; x) = -g_{16}(c_{16}, n+1; x) + (n - 1)g_{16}(c_{16}, n; x) \quad [185]$$

Instead of deriving explicitly the expansions with all the steps involved we restrict ourselves to listing the essential information about these expansions only.

The procedures are formally the same as the ones shown in detail deriving the expansions in ultraspherical polynomials and others. In the present case a detailed listing of intermediate results would generate many pages of tedious formulas however.

We can divide the generalized spheroidal DE through by a constant factor such that in [92] we have $a_2=1$ and we can scale x without loss of generality such that $b_2=\pm 1$, with the sign to be chosen depending on the type of expansion employed,

$$\underline{\underline{S}} Sw(x) = [(a_1 x + x^2) (d^2/dx^2) + (b_0 + b_1 x \pm x^2) (d/dx) + (k_0 + k_1 x)] Sw(x) = 0 . \quad [186]$$

Applying to this DE the properties of the basis functions of the expansions and furthermore choosing the parameters c_k such that an undesirable term vanishes, we find that we end up in all sixteen cases with a three-term recurrence relation among the expansion coefficients of [121]-[136],

$$\underline{\underline{S}} Sw_k(x) = \underline{\underline{S}} \sum_n q_{k,n} g_k(c_k | x) = 0 \quad [187]$$

$$\longrightarrow W_k^{(-)}(n) q_{k,n-1} + W_k^o(n) q_{k,n} + W_k^{(+)}(n) q_{k,n+1} = 0 \quad [188]$$

First we list the parameters c_k of the expansions :

$$c_1=c_2=c_9=c_{10} = b_0/a_1 \quad [189]$$

$$c_5=c_6=c_{13}=c_{14} = 2-(b_0/a_1) \quad [190]$$

$$c_3=c_4 = -k_1 \quad [191]$$

$$c_7=c_8 = 1-a_1-b_1-k_1 \quad [192]$$

$$c_{11}=c_{12} = a_1+b_1+k_1 \quad [193]$$

$$c_{15}=c_{16} = 1+k_1 \quad [194]$$

The differential operators of the generalized spheroidal wave functions to which the above relations for the expansion sets were applied are the following :

$$\underline{S} \equiv \begin{cases} [(a_1 x + x^2) (d^2/dx^2) + (b_0 + b_1 x - x^2) (d/dx) + k_0 + k_1 x] \\ \quad \text{for } k \leq 8 \\ [(a_1 x - x^2) (d^2/dx^2) + (b_0 - b_1 x - x^2) (d/dx) - k_0 + k_1 x] \\ \quad \text{for } k > 8 \end{cases} \quad [195]$$

The coefficients in the three-term recurrence relations as formulated in [188] are :

$$\underline{w_k^{(-)}(n)}$$

$$k=1 : \quad (n-1) (a_1 + b_1 + k_1 - c_1 + n - 1) \quad [196-a]$$

$$k=2 : \quad (n-1) (n - c_2) (a_1 + b_1 + k_1 - c_2 + n - 1) \quad [197-a]$$

$$k=3 : \quad (b_0 - a_1 (n-1)) (c_3 - n + 1) / (n-1) \quad [198-a]$$

$$k=4 : \quad a_1 (n-1) - b_0 \quad [199-a]$$

$$k=5 : \quad (n-1) (a_1 + b_1 + k_1 + n - 2) \quad [200-a]$$

$$k=6 : \quad (n-1) (n - c_6) (a_1 + b_1 + k_1 + n - 2) \quad [201-a]$$

$$k=7 : \quad (a_1 + b_1 + n - 3) (c_7 - n + 1) / (n-1) \quad [202-a]$$

$$k=8 : \quad 3 - n - a_1 - b_1 \quad [203-a]$$

$$k=9 : \quad (n-1) (n - k_1 - c_9 - 1) \quad [204-a]$$

k=10 :	$(n-1)(n-c_{10})(n-k_1-c_{10}-1)$	[205-a]
k=11 :	$(a_1(n-1)-b_0)(c_{11}-n+1)/(n-1)$	[206-a]
k=12 :	$b_0-a_1(n-1)$	[207-a]
k=13 :	$(n-1)(n-k_1-2)$	[208-a]
k=14 :	$(n-1)(n-c_{14})(n-k_1-2)$	[209-a]
k=15 :	$(a_1+b_1+n-3)(c_{15}-n+1)/(n-1)$	[210-a]
k=16 :	$c_{16}-a_1-b_1-k_1-n+2$	[211-a]

$$\underline{W_k^{\circ}(n)}$$

k=1 :	$n(2(c_1-k_1-n)-b_1)+k_1c_1+k_0$	[196-b]
k=2 :	$n(2(c_2-k_1-n)-b_1)+k_1c_2+k_0$	[197-b]
k=3 :	$(n-1)(n-a_1-b_1)+a_1(c_3-n)+b_0+k_0$	[198-b]
k=4 :	$(n-1)(n-a_1-b_1)+a_1(c_4-n)+b_0+k_0$	[199-b]
k=5 :	$c_5(b_1+k_1+2(n-1))-n(b_1+2(n+k_1))-b_1+2+k_0$	[200-b]
k=6 :	$c_6(b_1+k_1+2(n-1))-n(b_1+2(n+k_1))-b_1+2+k_0$	[201-b]
k=7 :	$(n-1)(b_1+n-2)+a_1c_7+k_0$	[202-b]
k=8 :	$(n-1)(b_1+n-2)+a_1c_8+k_0$	[203-b]
k=9 :	$(c_9-n)(2n-b_1-k_1)+nk_1+k_0$	[204-b]
k=10 :	$(c_{10}-n)(2n-b_1-k_1)+nk_1+k_0$	[205-b]
k=11 :	$(n-1)(n-b_1)-a_1(c_{11}-1)+k_0$	[206-b]
k=12 :	$(n-1)(n-b_1)-a_1(c_{12}-1)+k_0$	[207-b]
k=13 :	$(c_{13}-2n)(n-k_1-1)+(n-1)(c_{13}+b_1-2)+k_0$	[208-b]
k=14 :	$(c_{14}-2n)(n-k_1-1)+(n-1)(c_{14}+b_1-2)+k_0$	[209-b]
k=15 :	$(n-1)(n+b_1+2(a_1-1))-a_1c_{15}+b_0+k_0$	[210-b]
k=16 :	$(n-1)(n+b_1+2(a_1-1))-a_1c_{16}+b_0+k_0$	[211-b]

$$\underline{w_k^{(+)}(n)}$$

k=1	:	$(n+k_1+1)(n-c_1+1)$	[196-c]
k=2	:	k_1+n+1	[197-c]
k=3	:	$n(a_1+b_1-n-1)$	[198-c]
k=4	:	$(n+k_1)(a_1+b_1-n-1)$	[199-c]
k=5	:	$(n-c_5+1)(n+k_1-c_5+2)$	[200-c]
k=6	:	$n+k_1-c_6+2$	[201-c]
k=7	:	$n(b_0+a_1(n-1))$	[202-c]
k=8	:	$(n-c_8)(b_0+a_1(n-1))$	[203-c]
k=9	:	$(c_9-n-1)(a_1+b_1+k_1-n-1)$	[204-c]
k=10	:	$n+1-a_1-b_1-k_1$	[205-c]
k=11	:	$-n(n+1-a_1-b_1)$	[206-c]
k=12	:	$(n-c_{12})(c_{12}-k_1-n-1)$	[207-c]
k=13	:	$(c_{13}-n-1)(a_1+b_1+k_1+c_{13}-n-2)$	[208-c]
k=14	:	$n+2-a_1-b_1-k_1-c_{14}$	[209-c]
k=15	:	$-n(b_0+a_1(n-1))$	[210-c]
k=16	:	$(c_{16}-n)(b_0+a_1(n-1))$	[211-c]

Expansion of the Original GSW-DE in Confluent Hypergeometric Functions

If the original GSW-DE is expanded using the expansions proposed in [121]-[136] the following substitutions have to be made :

$$a_1 = 4p \quad [212]$$

$$b_0 = 4p(m+1) \quad [213]$$

$$b_1 = 2(m+1-2p) \quad [214]$$

$$k_0 = 2B+m(m+1)-p^2-A \quad [215]$$

$$k_1 = B/p \quad [216]$$

where

$$B = Q_{r,a} - p(m+1)$$

$$Q_r = \frac{1}{2}R(Z_1+Z_2) \quad , \quad Q_a = \frac{1}{2}R(Z_1-Z_2) \quad [217]$$

Independent of the substitutions to be made for a_1, b_0 etc., use of either Φ or Ψ functions will give rise to equal rates of convergence of the separation constant, i.e. identical truncated eigenvalue spectra. This becomes easily apparent from the fact that the diag. elements of the associated eigenvalue problems are equal in both cases. Of course the actual wave functions differ if a finite number of terms is considered.

The constants c_{1-16} in [121]-[136] according to [189]-[194] are :

$$c_1 = c_2 = c_9 = c_{10} = m+1 \quad [218]$$

$$c_5 = c_6 = c_{13} = c_{14} = 1-m \quad [219]$$

$$c_3 = c_4 = -(B/p) \quad [220]$$

$$c_7 = c_8 = -(2m+1+(B/p)) \quad [221]$$

$$c_{11} = c_{12} = 2(m+1)+(B/p) \quad [222]$$

$$c_{15} = c_{16} = 1+(B/p) \quad [223]$$

For the signs of p and R the four combinations shown in [73.5] are possible. Furthermore the algebraic eigenvalue problems associated with g_1 - g_{16} are intersected in two places if $m \neq 0$ leaving a sub-block of size $m \times m$ and two additional sub-blocks with infinite size. If $m=0$ only the latter are present. Performing numerical work it was found that in cases where the expansion index was the second parameter of the confluent hypergeom. functions, i.e.

$$Sw_k(x) = \sum_n q_n \cdots \Phi(c_k, n; x) \quad [224]$$

$$\text{or } Sw_k(x) = \sum_n q_n \cdots \Psi(c_k, n; x) \quad [225]$$

the angular spectra for the separation constant were generated. Exploring all of the eight such expansions and considering the four sign combinations for R and p eight different eigenvalue spectra were found, converging to the "angular eigenvalue spectrum" with eight different rates of convergence. An interesting fact is that all of the eight eigenvalue spectra can be found by taking one individual expansion, considering all four sign combinations and the upper and lower

infinite sub-blocks separately. For the case $m=0$ only four different eigenvalue spectra occur.

We recall that for the angular expansions in ultraspherical polynomials the choice of the signs of R and p had no effect on the rate of convergence of the eigenvalue spectrum. For the angular expansions in confluent hypergeom. functions the rate of convergence is by far inferior to the one found using expansions in ultraspherical polynomials. The table listing the number of significant figures of the separation constant generated by a 15-term expansion in confluent hypergeom. functions

$$S_w(x) \sim \sum_{n=2(m+1)}^{16} q_n \phi(c_3, n; x) \quad [226]$$

illustrates this if comparison is made with the tables following [73].

Fig II : The number of significant figures of the separation constant of the angular eigenfunction second lowest in energy with $m=0$ using a 15-term expansion in confluent hypergeometric functions as shown in [226].

Q_a	p	$-\sqrt{5}$	$-\sqrt{4}$	$-\sqrt{3}$	$-\sqrt{2}$	-1	0	1	$\sqrt{2}$	$\sqrt{3}$	$\sqrt{4}$	$\sqrt{5}$
9.5		8	8	9	10	12						
8.5		7	8	9	11	11						
7.5		6	7	8	9	11						
6.5		6	6	6	6	10						
5.5		4	4	6	8	10						
4.5		5	4	5	7	9						
3.5		2	3	5	6	8						
2.5		1	2	3	5	7						
1.5		0	1	2	3	6						
0.5		0	0	>16	2	4	0	0	0	0	0	
-0.5		>16	0	1	2	3	2	0	0	0	0	
-1.5							3	2	1	0	>16	
-2.5							5	1	1	0	0	
-3.5							6	2	0	1	0	
-4.5							6	3	1	0	0	
-5.5							7	4	1	0	>16	
-6.5							7	2	2	0	0	
-7.5							8	5	3	1	0	
-8.5							8	7	4	2	1	
-9.5							9	6	4	3	2	

The cases where the number of significant figures is indicated as ">16" are the ones for which the expansion is truncated (at less than 15 terms) due to a coefficient in the recurrence relation being zero.

If the first parameter of the confluent hypergeometric functions serves as expansion index the radial expansions are obtained. There are eight of the 16 expansions proposed in [121]-[136] of this type. The situation is similar to the one observed for the angular expansions in confluent hypergeometric functions. There is a total of four distinct eigenvalue spectra of the truncated radial expansions. Only two of them converge upon extending the number of terms considered in the expansion. All four of them can be generated taking one block of an arbitrarily chosen expansion in confluent hypergeometric functions considering the four possible combinations in sign for "R" and "p".

Unlike the angular expansions the finally converged eigenvalue spectra (the few lowest eigenvalues !) are distinct. The eigenvalue spectra of interest are the ones where the wave function remains bounded for $\lambda \rightarrow +\infty$.

This is the case if for the subblock for the polynomial solutions of the confluent hypergeometric DE the signs are chosen as follows :

$$p = |p| \quad ; \quad R = |R| \quad [227]$$

If, for a given combination of signs of R and p , the sign of p is changed then the eigenvalue spectrum of the infinite sub-block located opposite to the one considered in the first case will be identical to the original one. Hence if non-polynomial solutions of the confluent hypergeom. DE are employed in the expansion i.e. $n \geq 1$ the proper combination of signs will be the one obtained by changing the sign of p in [227]

$$p = -|p|, \quad R = |R| \quad [228]$$

The rate of convergence for this expansion is the same as the one of the Hylleraas and Jaffé expansion, although the generating function used by Hylleraas is not exactly the one of the Laguerre polynomials. The equivalence of his own expansion with a Laguerre polynomial expansion was apparently already known to Hylleraas. Four tables are given below listing the number of significant figures of the separation constant for different combinations of parameters of the GSW-DE. As was expected on the basis of qualitative speculations the rate of convergence is worst if " $|Q_r|p^2$ " is small. The picture becomes slightly distorted in a few cases where the ratio " Q_r/p " approaches a positive integer in which case near truncation of the expansion occurs. (We have actual truncation at the point $(p^2=1, Q_r=1)$).

Fig III : The number of significant figures of
the radial separation constant for the
 Σ -states:

- (i) $n=1$ with 7 terms
- (ii) $n=1$ with 21 terms
- (iii) $n=2$ with 7 terms
- (iv) $n=2$ with 21 terms

(i)

Q_r	p^2	.1	.2	.3	.4	.5	.6	.7	.8	.9	1.
.0		3	4	4	5	5	5	5	5	6	6
.1		3	4	4	5	5	5	5	6	6	6
.2		4	4	5	5	5	5	6	6	6	6
.3		5	5	5	5	5	6	6	6	6	6
.4		5	6	5	5	6	6	6	6	6	6
.5		5	5	6	6	6	6	6	6	6	7
.6		6	5	6	7	7	6	7	7	7	7
.7		6	6	6	6	9	7	7	7	7	7
.8		6	6	6	6	6	8	8	8	7	7
.9		7	9	6	6	6	6	8	10	8	8
1.		7	6	7	6	6	6	6	7	8	>16

(ii)

p^2	.1	.2	.3	.4	.5	.6	.7	.8	.9	1.
Q_r										
.0	7	8	9	10	10	11	11	11	12	12
.1	7	8	9	10	10	11	11	12	12	12
.2	8	9	9	10	11	11	11	12	12	12
.3	9	9	10	10	11	11	12	12	12	13
.4	8	10	10	11	11	12	12	12	13	13
.5	9	9	11	11	12	12	12	12	13	13
.6	10	10	11	12	12	12	13	13	13	13
.7	10	10	11	11	14	13	13	13	13	14
.8	10	11	11	11	12	14	14	14	14	14
.9	11	14	11	11	12	12	14	16	15	15
1.	12	11	12	12	12	12	13	14	15	>16

(iii)

p^2	.1	.2	.3	.4	.5	.6	.7	.8	.9	1.
Q_r										
.0	2	2	2	3	3	3	3	3	3	3
.1	2	2	2	3	3	3	3	3	3	3
.2	2	2	3	3	3	3	3	3	3	4
.3	2	2	3	3	3	3	3	3	4	4
.4	3	3	3	3	3	3	3	4	4	4
.5	3	3	3	3	3	3	4	4	4	4
.6	4	3	3	3	3	4	4	4	4	4
.7	4	4	3	4	4	4	4	4	4	4
.8	4	4	4	4	4	4	4	4	4	4
.9	5	7	4	4	4	4	4	4	4	4
1.	5	4	5	4	4	4	4	4	4	4

(iv)

p	.1	.2	.3	.4	.5	.6	.7	.8	.9	1.
Q_r										
.0	5	6	7	7	8	8	8	9	9	9
.1	5	6	7	7	8	8	9	9	9	9
.2	5	6	7	7	8	8	9	9	9	10
.3	6	7	7	8	8	8	9	9	9	10
.4	6	7	7	8	8	9	9	9	10	10
.5	7	7	8	8	8	9	9	9	10	10
.6	8	7	8	8	9	9	9	10	10	10
.7	7	8	8	9	9	9	9	10	10	10
.8	8	9	9	9	9	9	10	10	10	10
.9	9	11	9	9	9	10	10	10	10	10
1.	10	8	10	10	10	10	10	10	10	11

Tables of the actual numerical values of separation constants for the cases listed are provided in appendix II.

Since Laguerre polynomials are related to Hermite polynomials as follows :

$$H_{2n}(x) = (-1)^{2n} \Gamma(n+1) L_n^{-\frac{1}{2}}(x^2) \quad [229]$$

$$H_{2n+1}(x) = (-1)^{2n+1} \Gamma(n+1) x L_n^{\frac{1}{2}}(x^2) \quad [230]$$

one might suspect that expansions in terms of Hermite polynomials and functions would generate the radial solutions to the GSW-DE.

Looking for expansions :

$$\sum_n q_n^{(1)} \{ (x^2 - p^2) D^2 + 2(m+1)xD - x^2 + m(m+1) - A \} H_{2n}(x) = 0 \quad [231]$$

$$\sum_n q_n^{(2)} \{ (a_1 x + x^2) D^2 + (b_0 + b_1 x - x^2) D + k_0 + k_1 x \} H_n(x) = 0 \quad [232]$$

using the relations,

$$\begin{aligned} x^2 D^2 H_n(x) &= n(n-1) [H_n(x) + 2(2n-3)H_{n-2}(x) \\ &\quad + 4(n-3) {}_2H_{n-4}(x)] \end{aligned} \quad [233]$$

$$xD^2 H_n(x) = 2(n-1) {}_2[H_{n-1}(x) + 2(n-2)H_{n-3}(x)] \quad [234]$$

$$D^2 H_n(x) = 4(n-1) {}_2H_{n-2}(x) \quad [235]$$

$$\begin{aligned} x^2 D H_n(x) &= n \left[\left(\frac{1}{2}\right) H_{n+1}(x) + (2n-1) H_{n-1}(x) \right. \\ &\quad \left. + 2(n-2) {}_2H_{n-3}(x) \right] \end{aligned} \quad [236]$$

$$xD H_n(x) = n [H_n(x) + 2(n-1)H_{n-2}(x)] \quad [237]$$

$$D H_n(x) = 2n H_{n-1}(x) \quad [238]$$

$$\begin{aligned} x^2 H_n(x) &= \left(\frac{1}{4}\right) H_{n+2}(x) + \left(n + \left(\frac{1}{2}\right)\right) H_n(x) \\ &\quad + (n-1) {}_2H_{n-2}(x) \end{aligned} \quad [239]$$

$$x H_n(x) = \left(\frac{1}{2}\right) H_{n+1}(x) + n H_{n-1}(x) \quad [240]$$

one readily obtains recurrence relations for the expansion coefficients in [231] and [232] :

$$\begin{aligned} & - \left(\frac{1}{4}\right) q_{n-2}^{(1)} + [m(2n+m+1) + n^2 - \left(\frac{1}{2}\right) - A] q_n^{(1)} \\ & + [(n+1) {}_2(4(n+m-p^2)+5)] q_{n+2}^{(1)} + [4(n+1) {}_4] q_{n+4}^{(1)} = 0 \end{aligned} \quad [241]$$

$$\begin{aligned} & q_{n-1}^{(2)} \left[\left(\frac{1}{2}\right) (k_1 - n + 1) \right] + q_n^{(2)} [n(n+b_1-1) + k_0] + q_{n+1}^{(2)} [(n+1) \\ & (2(b_0 + n(a_1-1)) + k_1 - 1)] + q_{n+2}^{(2)} [2(n+1) {}_2(2n+b_1+1)] \\ & + q_{n+3}^{(2)} [2(n+1) {}_3(2a_1-1)] + q_{n+4}^{(2)} [4(n+1) {}_4] = 0 \end{aligned} \quad [242]$$

In [242] the substitutions listed in [212]-[217] would have to be made. The eigenvalue spectra derived from [241] and [242] are the ones of the angular eigenfunctions. For moderate p^2 they were found to be very slowly convergent. Using a 15-term expansion in [231] for different Q_a 's and p 's it was found in general that more than half the eigenvalues of the obtained spectra were complex conjugate pairs. This constitutes further evidence for slow convergence of these expansions making them entirely unattractive for the use in numerical work.

From Fig. II it is apparent that the expansion in [226] converges faster with increasing internuclear distance which indicates a possible usefulness of the angular expansions in confluent hypergeom. functions if corresponding sections of the potential energy curve of a heteronuclear species are to be explored.

Jaffé Expansions for the GSW-DE

A bilinear transform like the one used by Jaffé can be applied to any GSW-DE :

$$\{(x^2+a_1x)D^2+(b_0+b_1x+b_2x^2)D+k_0+k_1x\} y(x) = 0 \quad [243]$$

This transform is achieved in three individual steps as shown below. First we divide out an arbitrary power of x

$$j(x) = x^{-\alpha} y(x) \quad [244]$$

which transforms [243] into :

$$\begin{aligned} &\{x^2(x+a_1)D^2+x[2\alpha a_1+b_0+(b_1+2\alpha)x+b_2x^2]D+(k_1+\alpha b_2)x^2 \\ &+[\alpha(b_1+\alpha-1)+k_0]x+\alpha[(\alpha-1)a_1+b_0]\} j(x) = 0 \end{aligned} \quad [245]$$

Then α is chosen such that the quadratic term in the coefficient of j in [245] vanishes

$$\alpha = -k_1/b_2 \quad [246]$$

Substituting for the variable

$$x = t^{-1} \quad [247]$$

[245] transforms into

$$\begin{aligned} &\{t^2(1+a_1t)D^2-[(2(\alpha-1)a_1+b_0)t^2+(b_1+2(\alpha-1))t+b_2]D \\ &+[\alpha((\alpha-1)a_1+b_0)]t+\alpha(b_1+\alpha-1)+k_0\} j(t) = 0 \end{aligned} \quad [248]$$

Making the additional substitution

$$t = (s-1)/a_1 \quad [249]$$

the last DE transforms into :

$$\{s(s-1)^2 D^2 - [(2(\alpha-1)+T_0)s^2 + (b_1 - 2(T_0+\alpha-1))s + a_1 b_2 - b_1 + T_0]D + \alpha[T_0+\alpha-1]s + \alpha(b_1 - T_0) + k_0\} j(s) = 0$$

where $T_0 = b_0/a_1$ [250]

A power series expansion for j

$$j(s) = \sum_n q_n s^n \quad [251]$$

is defined by the three-term recurrence relation among its expansion coefficients

$$q_{n-1}[(n-1)(n-2\alpha-T_0) + \alpha(T_0+\alpha-1)] + q_n[n(2(T_0+\alpha-n)-b_1) + \alpha(b_1-T_0) + k_0] + q_{n+1}[(n+1)(n+b_1-a_1 b_2 - T_0)] = 0 \quad [252]$$

which was obtained by substituting [251] into [250] and applying standard procedures. Notice that the indicial equation of [250] has roots

$$r_1 = 0, \quad r_2 = T_0 + a_1 b_2 - b_1 + 1 \quad [253]$$

If for [250] we assume a Frobenius type solution

$$j(s) = \sum_n q_n s^{n+\beta} = s^\beta h(s) \quad [254]$$

[250] transforms into

$$\{s^2(s-1)^2 D^2 + s[(2(\beta-\alpha+1)-T_0)s^2 + (2(T_0+\alpha-2\beta-1)-b_1)s + 2\beta - a_1 b_2 + b_1 - T_0]D + [\beta(\beta-2\alpha+1-T_0) + \alpha(T_0+\alpha-1)]s^2 + [\alpha(b_1-T_0) - \beta(2(\beta-T_0-\alpha)+b_1) + k_0]s + \beta(\beta - a_1 b_2 + b_1 - T_0 - 1)\} h(s) = 0 \quad [255]$$

For h we can have power series expandable solutions if

$$\beta = \begin{cases} \beta_1 = 0 \\ \beta_2 = T_0 + a_1 b_2 - b_1 + 1 \\ \beta_3 = \alpha + T_0 \\ \beta_4 = \alpha + 1 \end{cases} \quad [256]$$

and they are defined by the following recurrence relation among their expansion coefficients :

$$\begin{aligned} & q_{n-1} [n(2\beta - a_1 b_2 + b_1 + n - 1 - T_0) + \beta(\beta - a_1 b_2 + b_1 - T_0 - 1)] \\ & + q_n [n(2(T_0 + \alpha - 2\beta - n) - b_1) + \alpha(b_1 - T_0) - \beta(2(\beta - T_0 - \alpha) + b_1) + k_0] \\ & + q_{n+1} [n(n+1 - T_0 + 2(\beta - \alpha)) + \beta(\beta - 2\alpha + 1 - T_0) + \alpha(T_0 + \alpha - 1)] = 0 \end{aligned} \quad [257]$$

Feasibility Study for the Frobenius-Jaffé

Type Expansions

Examining the limiting form of the radial expansions for $R \rightarrow 0$ presented in [29] we realize that the radial wave functions might asymptotically approach non-integer powers in the neighbourhood of the expansion center for small R .

In this situation rapid rate of convergence can be expected to occur if at the expansion center the expansion terms (or at least one of them) show the same asymptotic behaviour.

Jaffé did not mention that his DE had an indicial equation with roots differing by a non-integer number. Apparently he rejected Frobenius type solutions for physical reasons, i.e., the shape of the radial wave functions at the nuclei for $m=0$.

It can be shown that a non-integer power at the expansion center can be generated with a Jaffé type expansion. In this case it would do no harm in respect to physical acceptability if a non-integer power is factored out. To show what is meant by the above statement we can examine the second order equidimensional DE

$$\{x^2 (d^2/dx^2) + ax (d/dx) + b\} g(x) = 0 \quad [258]$$

having a char. polynomial with the pair of roots

$$r_{1,2} = [\frac{1}{2}(1-a)] \pm \sqrt{[\frac{1}{2}(a-1)]^2 - b} \quad [259]$$

Substituting for the variable

$$s = x/(x+2) \quad [260]$$

transforms [258] into

$$\{s^2 (s-1)^2 D^2 + s(s-1)(2s-a)D + b\} g(s) = 0 \quad [261]$$

a DE which has an indicial equation with the same roots as the indicial equation of [258], i.e. the pair of roots shown in [259].

A power series expansion for g

$$g(s) = \sum_n q_n s^n \quad [262]$$

is defined by the following recurrence relation :

$$q_{n-1}[n^2-1] - q_n[n(2(n+1)+a)] + q_{n+1}[n^2+n(2+a)+(2+b)] = 0 \quad [263]$$

Notice that in the tridiag. (tridiagonal) matrix corresponding to this recurrence relation the diag. elements grow with " $-2n^2$ " whereas the upper and lower off-diag. elements grow with " n^2 ". The same is the case for the radial expansion in confluent hypergeom. functions and the Jaffé type expansions.

This is an indication that these expansions actually do build up a non-integer power at the expansion center.

Notice as well that non-integer powers and logarithmic functions can be expanded in confluent hypergeometric functions :

$$x^\alpha = \Gamma(a+\alpha+1) \sum_n [(-\alpha)_n / \Gamma(a+n+1)] L_n^a(x) \quad [264]$$

$$0 \leq n < \infty, \quad -\alpha < 1 + \min(a, \frac{1}{2}a - \frac{1}{4})$$

$$\ln(x) = \psi(a+1) - \Gamma(a+1) \sum_{n=1}^{\infty} [\Gamma(n) / \Gamma(a+n+1)] L_n^a(x) \quad [265]$$

Jaffé Expansions of the Original GSW-DE

If in [256] we make the substitutions [212]-[216] and [250] and taking $b_2=-1$ we get :

$$\beta_1 = 0 \quad [266]$$

$$\beta_2 = -m \quad [267]$$

$$\beta_3 = (B/p)+m+1 \quad [268]$$

$$\beta_4 = (B/p)+1 \quad [269]$$

The pairs β_1, β_2 and β_3, β_4 differ by "m" which is an integer. Hence the expansion of [255] with $\beta=\beta_1$ is equivalent to the one with $\beta=\beta_2$ if we just replace the expansion index "n" by "n-m" and the same relationship applies to the pair β_3, β_4 .

In the original GSW-DE as for example written in [18] replacing "R" by "-R" is equivalent to changing the sign of the variable. From the form of the Jaffé expansion as shown in [48] it can easily be seen that taking $\beta_4=\alpha+1$ (or $\beta_4=\sigma+1$ if referred to [48]) is equivalent to changing the sign of "R" and taking expansions with $\beta=\beta_1$ or equivalently $\beta=\beta_2$.

Hence due to the six coefficients in [243] being interrelated by only three parameters R, m and E_e we have actually no additional option if we resort to Frobenius expansions of [255].

The table below summarizes this situation. The eigenvalue spectra are designated with $\{A\}_k$ with $k=1,2,3,4$.

k	β_1	β_2	β_3	β_4
$p=- p $, $R=- R $	1	1	$2^\dagger$	$2^\dagger$
$p=- p $, $R= R $	2	2	$1^\dagger$	$1^\dagger$
$p= p $, $R=- R $	3	3	$4^\dagger$	$4^\dagger$
$p= p $, $R= R $	4	4	$3^\dagger$	$3^\dagger$

$\{A\}_1$ is the eigenvalue spectrum of the physically meaningful eigenfunctions of the radial GSW-DE.

The matrices arising from β_3 and β_4 are the transpose of the ones obtained using β_1 and β_2 . This is indicated by the " $\dagger$'s". This notation holds throughout.

CHAPTER III

Integral Transforms

It is a well-known fact that integral transforms have played an important role in the investigations and solutions of many different types of DE's.

In the present case the wave function would simply be the preimage of the expansion of the transformed GSW-DE. One would expect that if we guarantee the existence of the integral transform by formulating an algebraic eigenvalue problem as before, in the case of convergence for a given set of parameters R, p and m , we guarantee simultaneously the existence of the preimage of this expansion. In other words, the same eigenvalue spectra are expected to occur when working with integral transforms as by expanding the original wave function.

The Laplace Transform of the GSW-DE

It can be shown that by a Laplace transform a GSW-DE is transformed to a GSW-DE.

We are interested in the following transformation

$$\begin{aligned} \mathfrak{L}\{\underline{S}[L(\lambda)] | s\} &= \mathfrak{L}\{[(\lambda^2-1)D^2+2\lambda(m+1)D-(p\lambda)^2 \\ &\quad +2Q\lambda+m(m+1)-A]L(\lambda) | s\} = 0 \end{aligned} \quad [270]$$

where according to the distinction between an angular and a radial expansion the following ambiguity of sign occurs :

$$Q = \frac{1}{2}(Z_1 \pm Z_2)R \quad [271]$$

The Laplace transform of the wave function which we write as $\ell(s)$ satisfies the Laplace transformed DE in [270]. The transforms of the individual terms are

$$\begin{aligned} &\mathfrak{L}\{(\lambda^2-1)D^2L(\lambda) | s\} \\ &= (d^2/ds^2)[s^2\ell(s)-sL(0)-L'(0)]-s^2\ell(s)+sL(0)+L'(0) \end{aligned} \quad [272]$$

$$\mathfrak{L}\{2\lambda(m+1)DL(\lambda) | s\} = -2(m+1)(d/ds)[s\ell(s)-L(0)] \quad [273]$$

$$\begin{aligned} & \mathcal{L}\{[-(p\lambda)^2 + 2Q\lambda + m(m+1) - A]L(\lambda) | s\} \\ &= [-p^2(d^2/ds^2) - 2Q(d/ds) + (m(m+1) - A)]\ell(s) \end{aligned} \quad [274]$$

The transformed GSW-DE then becomes

$$\begin{aligned} & \{(s^2 - p^2)D^2 - 2((m-1)s + Q)D + [-s^2 + m(m-1) - A]\}\ell(s) \\ &= -[sL(0) + L'(0)] \end{aligned} \quad [275]$$

for which we seek the homogeneous solution.

Applying the transformations

$$\ell_h(s) = \exp(s)g_1(s) \quad [276]$$

$$\ell_h(s) = \exp(-s)g_2(s) \quad [277]$$

one obtains a pair of DE's :

$$\begin{aligned} & \{(s^2 - p^2)D^2 - 2[s^2 + (m-1)s + (Q - p^2)]D \\ & + [2(m-1)s + m(m-1) + 2Q - p^2 - A]\}g_1(s) = 0 \end{aligned} \quad [278]$$

$$\begin{aligned} & \{(s^2 - p^2)D^2 + 2[s^2 - (m-1)s - (Q + p^2)]D \\ & + [2(1-m)s + m(m-1) - 2Q - p^2 - A]\}g_2(s) = 0 \end{aligned} \quad [279]$$

Shifting the center of expansion

$$2x = s \pm p \quad [280]$$

where we choose the plus sign. This available choice is equivalent to choosing the sign of p , an option available to us for the original GSW-DE as well.

$$\begin{aligned} & \{x(x-4p)D^2 - [x^2 + 2(m-1-2p)x + 4(Q - (m-1)p)]D \\ & + [(m-1)x + (m-1)(m-2p) + 2Q - p^2 - A]\}g_1(x) = 0 \end{aligned} \quad [281]$$

$$\begin{aligned} & \{x(x-4p)D^2 + [x^2 - 2(m-1+2p)x - 4(Q - (m-1)p)]D \\ & + [(1-m)x + (m-1)(m+2p) - 2Q - p^2 - A]\}g_2(x) = 0 \end{aligned} \quad [282]$$

The last two DE's are equivalent : [282] can be obtained from [281] by changing the signs of p and R and the variable x . A power series expansion for g_1

$$g_1(x) = \sum_n q_n x^n \quad [283]$$

is defined by the three-term recurrence relation holding among the q_n 's

$$\begin{aligned} q_{n-1} [m-n] + q_n [n(n-2m+4p) + (m-2p)(m-1) + 2Q - p^2 - A] \\ = 4q_{n+1} [(n+1)(Q+p(n-m+1))] \end{aligned} \quad [284]$$

The expansion terms can be back-transformed if for the expansion index the following is specified :

$$-1 \leq n < -\infty \quad [285]$$

which gives

$$\mathfrak{f}^{-1}\{s^{-n}|x\} = x^{(n-1)}/\Gamma(n) \quad [286]$$

For inverse Laplace transforms in general the following holds :

$$\mathfrak{f}^{-1}\{a_1 f_1(s) + a_2 f_2(s) | x\} = a_1 \mathfrak{f}^{-1}\{f_1(s) | x\} + a_2 \mathfrak{f}^{-1}\{f_2(s) | x\} \quad [287]$$

However if the sum has infinitely many terms this procedure, being a combination of two limiting processes, becomes problematic. Nevertheless it is believed that, if the eigenvalue spectra of the expansion of the Laplace transformed wave functions converge, then existence of the inverse Laplace

transforms of all expansion terms is sufficient to assure that what is obtained by term-by-term back-transformation represents the Laplace preimage of this expansion.

A nice example where we find a rapidly converging angular eigenvalue spectrum but cannot achieve term-by-term back-transformation is an expansion in Jacobi polynomials shown below.

For an expansion of [278] (and [279]) in Jacobi polynomials the following relations are needed :

$$\begin{aligned} (2n+\alpha+\beta) {}_3xP_n^{(\alpha,\beta)}(x) &= 2(n+1)(n+\alpha+\beta+1)(2n+\alpha+\beta)P_{n+1}^{(\alpha,\beta)}(x) \\ &- (2n+\alpha+\beta+1)(\alpha^2-\beta^2)P_n^{(\alpha,\beta)}(x) - 2(n+\alpha)(n+\beta) \\ &(2n+\alpha+\beta+2)P_{n-1}^{(\alpha,\beta)}(x) \end{aligned} \quad [288]$$

$$\begin{aligned} (2n+\alpha+\beta)(1-x^2)(d/dx)P_n^{(\alpha,\beta)}(x) &= [\alpha-\beta-(2n+\alpha+\beta)x]P_n^{(\alpha,\beta)}(x) \\ &+ 2(n+\alpha)(n+\beta)P_{n-1}^{(\alpha,\beta)}(x) \end{aligned} \quad [289]$$

and the linear differential operator satisfied by the Jacobi polynomials ,

$$\{(1-x^2)D^2 + [\beta-\alpha-(\alpha+\beta+2)x]D + n(n+\alpha+\beta+1)\} P_n^{(\alpha,\beta)}(x) = 0 \quad [290]$$

The parameters α and β were chosen such that bothersome terms vanished as follows :

$$\alpha = -(m+(Q/p)) \quad [291]$$

$$\beta = -(m-(Q/p)) \quad [292]$$

The expansion ,

$$g_1(s/p) = \sum_n q_n P_n^{(\alpha, \beta)}(s/p) \quad [293]$$

if substituted into [278] generates the following recurrence relation for the q_n 's :

$$\begin{aligned} & q_{n-1} [2np(2m-n)/(2(n-m)-1)] + q_n [n(n-2m+1)+m(m-1)-p^2-A] \\ & = q_{n+1} [2p((Q/p)^2-(n-m+1)^2)/(2(n-m)+3)] \end{aligned} \quad [294]$$

The truncated characteristic polynomials derived from [294] are the same as for the expansion in ultraspherical polynomials which themselves are special cases of Jacobi polynomials,

$$\begin{aligned} C_n^{(a+\frac{1}{2})}(x) &= [[\Gamma(a+1)\Gamma(2a+n+1)]]/[[\Gamma(2a+1)\Gamma(a+n+1)]] \\ &P_n^{(a,a)}(x) \end{aligned} \quad [295]$$

The Jacobi polynomials do not have inverse Laplace transforms. If one chooses,

$$-1 \leq n < -\infty \quad [296]$$

the Jacobi functions can be formulated as generalized hypergeometric functions :

$$\begin{aligned} P_n^{(\alpha, \beta)}(x) &= [[(\alpha+1)_n/\Gamma(n+1)]] {}_2F_1(-n, \alpha+\beta+n+1; \alpha+1; \\ &(1-x)/2) \end{aligned} \quad [297]$$

If we make use of the well-known linear transformation formula,

$$\begin{aligned}
& {}_2F_1(-n, \alpha+\beta+n+1; \alpha+1; (1-x)/2) = ((1+x)/2)^n \\
& \{ [\Gamma(\alpha+1)\Gamma(2n+\alpha+\beta+1)] / [\Gamma(\alpha+\beta+n+1)\Gamma(\alpha+n+1)] \} \\
& {}_2F_1(-n, -(n+\beta); -(2n+\alpha+\beta); 2/(1+x)) + ((1+x)/2)^{-(\alpha+\beta+n+1)} \\
& \{ [\Gamma(\alpha+1)\Gamma(-(2n+\alpha+\beta+1))] / [\Gamma(-n)\Gamma(-(n+\beta))] \} \\
& {}_2F_1(\alpha+\beta+n+1, \alpha+n+1; 2n+\alpha+\beta+1; 2/(1+x)) \quad [298]
\end{aligned}$$

and using the formula ,

$$\begin{aligned}
& \mathfrak{L}^{-1}\{x^{-\sigma} {}_2F_1(a_1, a_2; b_1; 2/x) | t\} = [t^{\sigma-1}/\Gamma(\sigma)] \\
& {}_2F_2(a_1, a_2; b_1, \sigma; 2t) \quad , \quad \text{Re}(\sigma) > 0 \quad [299]
\end{aligned}$$

and the shift theorem of the Laplace transform, one encounters further difficulties since, for the second term in [298], the restriction for σ in [299] does not hold if n is chosen as shown in [296].

The roots of the indicial equations of [281] and [282] in general differ by a non-integer number.

They are :

$$r_1 = 0 \quad ; \quad r_2 = m - (Q/p) \quad [300]$$

We substitute in [281] ,

$$h(x) = x^{(m-T)} g_1(x) \quad [301]$$

where the substitution " $T=Q/p$ " is made throughout this section.

Then [281] becomes ,

$$\begin{aligned}
& \{x(x-4p)D^2 - [x^2 + 2(T-2p-1)x - 4(Q-p(m+1))]D + [(T-1) \\
& (T+x-2p) + 2mp - p^2 - A]\} h(x) = 0 \quad [302]
\end{aligned}$$

A power series expansion of h ,

$$h(x) = \sum_n q_n (x/2)^n \quad [303]$$

is defined by the following three-term recurrence relation :

$$\begin{aligned} 2q_{n-1}[T-n] + q_n[n(n+1-2T+4p)+2mp+(T-2p)(T-1)-p^2-A] \\ + 2q_{n+1}[(n+1)(Q-p(n+m+1))] = 0 \end{aligned} \quad [304]$$

Two distinct eigenvalue spectra can be obtained from the last expression depending on the choice of the signs of R and p . The same eigenvalue spectra are obtained if from the original GSW-DE,

$$\begin{aligned} \{x(x-2)D^2 - 2[px^2 - (2p+m+1)x + (m+1)]D + 2[Q-p(m+1)]x \\ + [m(m+1) - 2(Q-p(m+1)) - p^2 - A]\} g_3(x) = 0 \end{aligned} \quad [305]$$

a power is factored out ,

$$g_3(x) = x^{(T-m-1)} h_1(x) \quad [306]$$

which gives ,

$$\begin{aligned} \{x^2(x-2)D^2 - 2[px^2 - (T+2p)x + (2T-m-1)]xD + [(T-m-1) \\ (T+m+2p) + m(m+1) - p^2 - A]x - 2(T-1)(T-m-1)\} h_1(x) = 0 \end{aligned} \quad [307]$$

A power series expansion of h_1 ,

$$h_1(x) = \sum_n q_n x^n \quad [308]$$

is defined by the following recurrence relation :

$$\begin{aligned} -2[(n-1)p]q_{n-1} + [n[2(T+2p)+n-1] + (T-m-1)(T+m+2p) \\ + m(m+1) - p^2 - A]q_n - 2[(n+1)(2T+n-m-1) + (T-1)(T-m-1)]q_{n+1} \end{aligned}$$

$$= 0$$

[309]

One eigenvalue spectrum of [309] is obtained if the signs for p and Q are the same and a distinct one is found if these signs differ. The two eigenvalue spectra although being convergent apparently are physically meaningless.

Since a Laplace transform generates a GSW-DE from a GSW-DE, one is tempted to explore "higher generations" of integral transforms. For example writing [302] ,

$$\{ (1 - (4p/x))D^2 - [1 + [2(T-2p-1)/x] - [4(Q-p(m+1))/x^2]]D \\ + [(T-1)/x] + [(T-1)(T-2p) + 2mp - p^2 - A]/x^2 \} h(x) = 0$$

[310]

and taking an inverse Laplace transform ,

$$\mathcal{L}^{-1}\{h(x) | s\} = \ell(s)$$

gives the following integral equation :

$$\{s(s+1)\ell(s) - \int_0^s [4pt^2 - 2(T-1-2p)t - (T-1)]\ell(t) dt \\ - \int_0^s \int_0^s [4(Q-p(m+1))t + (T-1)(T-2p) + 2mp - p^2 - A] \\ \ell(t) (dt)^2 \} = 0$$

[311]

Taking twice the derivative gives the DE :

$$\{s(s+1)D^2 + [T+1+2s(T+1-2p) - 4ps^2]D - 4(Q-p(m-1))s \\ + (T+1)(T-2p) + 2mp - p^2 - A\} \ell(s) = 0$$

[312]

If from the original GSW-DE one takes twice the Laplace transform the original GSW-DE is obtained

with the sign of the variable changed.

If in [270] we make the substitutions

$$t = \exp(a\lambda) \quad [313]$$

$$(d/d\lambda) = at(d/dt) \quad [314]$$

$$(d/d\lambda)^2 = a^2(t^2(d/dt)^2 + t(d/dt)) \quad [315]$$

we are dealing with equidimensional linear differential operators. Then making use of the following two general properties of the Mellin transform :

$$M\{(x(d/dx))^n \phi(x) | z\} = (-z)^n M\{\phi(x) | z\} \quad [316]$$

$$M\{(\ln(x))^n \phi(x) | z\} = (d/dz)^n M\{\phi(x) | z\} \quad [317]$$

we can generate a second order linear DE with polynomials as coefficients from [270].

The Mellin transform of ϕ is given by

$$M\{\phi(x) | z\} = \int_0^\infty x^{z-1} \phi(x) dx \quad [318]$$

and it is related to the Laplace transform, which is apparent upon performing the simple substitution

$$t = -\ln(x) \quad [319]$$

which gives a two-sided Laplace transform

$$M\{\phi(x) | z\} = \int_{-\infty}^\infty (e^{-t}) e^{-tz} dt \quad [320]$$

or equivalently a sum of two one-sided Laplace

integrals of parameter z and $-z$

$$M\{\phi(x) | z\} = \int_0^\infty \phi(e^{-t}) e^{-tz} dt + \int_0^\infty \phi(e^t) e^{-t(-z)} dt \quad [321]$$

After performing the substitutions listed in [313]-[315] the limiting factor of the Mellin preimage will be

$$L(t) \sim t^{(p/a)} ; \quad |t| \rightarrow \infty \quad [322]$$

and [270] becomes

$$\begin{aligned} & \{ [\ln^2(t) - a^2] (tD)^2 + 2 \ln(t) (m+1) (tD) \\ & - (p/a)^2 \ln^2(t) + 2(Q/a) \ln(t) + m(m+1) - A \} L(t) = 0 \end{aligned} \quad [323]$$

Denoting the Mellin transform of the wave function

$$M\{L(t) | s\} = g(s) \quad [324]$$

the transform satisfies :

$$\{ (s^2 - p^2) D^2 - 2[(m-1)s - Q] D - s^2 + m(m+1) - A \} g(s/a) = 0 \quad [325]$$

which is the same as the Laplace transform [275] except for the sign of Q .

Expansion of the Laplace Image in Confluent Hypergeometric Functions

In the previous section it was shown that the Laplace transformed GSW-DE is itself a GSW-DE. Since the expansion in confluent hypergeom. functions were worked out for a GSW-DE with unspecified coefficients, the recurrence relations [196]-[211] can be applied.

First the inverse Laplace transforms of the expansion terms will be examined. We need essentially four back-transforms to cover all the expansions proposed, if the original Laplace transformed GSW-DE's [281] and [282] are expanded.

Expanding [302], where a power corresponding to the non-zero root of the indicial equation was factored out, two additional inverse Laplace transforms have to be evaluated. The exponential factors occurring in the expansions are taken care of by simply employing the shift theorem of the inverse Laplace transform.

From the literature by standard mathematical operations (7,*) we extract readily the following result :

$$\mathcal{L}^{-1}\{\Psi(\alpha, \gamma; s) | t\} = [(1+t)^{(\gamma-2)} / \Gamma(\alpha)] [t/(1+t)]^{(\alpha-1)}$$

$$\text{Re}(\alpha) > 0 \quad , \quad \text{Re}(s) > 0 \quad [326]$$

(*) Vol. I, p.269 ; #4

If the exponential factor of the expansion is taken into account we find that term-by-term back-transformation of the expansion according to [326] the familiar Jaffé expansion is obtained. From this we gain some understanding regarding the initially perplexing equivalence of the convergence rates of these entirely different expansions.

The remaining three inverse Laplace transforms are :

$$\mathfrak{L}^{-1}\{\Phi(\alpha, \gamma; s) | t\} = t^{-1} {}_2F_1(\alpha, 1; \gamma; t^{-1}) \quad [327]$$

$$\begin{aligned} \mathfrak{L}^{-1}\{s^{(\gamma-1)} \Psi(\alpha, \gamma; s) | t\} &= [t^{(\alpha-\gamma)} / \Gamma(\alpha-\gamma+1)] {}_1F_0(\alpha; ; -t) \\ &= [t^{(\alpha-\gamma)} / \Gamma(\alpha-\gamma+1)] \sum_{n=0}^{\infty} [(\alpha)_n / (1)_n] (-t)^n \\ &= [t^{(\alpha-\gamma)} / \Gamma(\alpha-\gamma+1)] (1+t)^{-\alpha} \quad \text{Re}(\alpha-\gamma+1) > 0, \text{Re}(s) > 0 \end{aligned} \quad [328]$$

$$\mathfrak{L}^{-1}\{s^{(\gamma-1)} \Phi(\alpha, \gamma; s) | t\} = [\Gamma(\gamma) / t^\gamma] [t-1]^{-\alpha} \quad [329]$$

The last two formulas indicate again a Jaffé expansion as the Laplace preimage of an expansion in confluent hypergeom. functions.

The inverse Laplace transforms above were derived from tables of Laplace transforms by Oberhettinger and Badii⁽⁸⁾ making proper substitutions.

Finally we consider the two additional cases arising from confluent hypergeom. expansions of [302].

From literature^(7,*)

$$\mathfrak{L}^{-1}\{s^u \Psi(\alpha, \gamma; s) | t\} = [t^{\alpha-u-1} / \Gamma(\alpha-u)] {}_2F_1(\alpha, \alpha-\gamma+1; \alpha-u; -t) \quad [330]$$

and^(8,**)

$$\mathfrak{L}^{-1}\{s^{-u} \Phi(\alpha, \gamma; s^{-1}) | t\} = {}_1F_2(\alpha; \gamma, u; t) \quad [331]$$

For the inverse Laplace transform the following holds^(8,***) :

$$\mathfrak{L}^{-1}\{s^{-1} g(s^{-1}) | t\} = \int_0^\infty \mathfrak{L}^{-1}\{g(s) | u\} J_0(2\sqrt{ut}) \, du \quad [332]$$

Applying this to [331] gives

$$\begin{aligned} \mathfrak{L}^{-1}\{s^{(u-1)} \Phi(\alpha, \gamma; s) | t\} &= [1/\Gamma(u)] \\ &\int_0^\infty u^{(u-1)} J_0(2\sqrt{ut}) {}_1F_2(\alpha; \gamma, u; u) \, du \\ &= [t^{-u}/\Gamma(u)] \int_0^\infty y^{(u-1)} J_0(2\sqrt{y}) {}_1F_2(\alpha; \gamma, u; y/t) \, dy \\ &\quad y = ut \end{aligned} \quad [333]$$

which is simply a Hankel transform. Using the formalism of Meijer's G-function [333] becomes^(7,****)

$$\begin{aligned} \mathfrak{L}^{-1}\{s^{(u-1)} \Phi(\alpha, \gamma; s) | t\} &= [\Gamma(\gamma)/\Gamma(\alpha)] t^{-u} \\ &\int_0^\infty y^{(u-1)} J_0(2\sqrt{y}) G_{1,3}^{1,1}\left(y/t \left| \begin{matrix} 1-\alpha \\ 0, 1-\gamma, 1-u \end{matrix} \right. \right) dy \end{aligned}$$

(*) Vol. I, p. 270

(**) p. 407, #19.15

(***) p. 209, # 1.20

(****) Vol. I, p.214, #9

$$\begin{aligned}
&= [\Gamma(\gamma)/\Gamma(\alpha)] t^{-\nu} G_{3,3}^{1,2} \left(t^{-1} \middle| \begin{matrix} 1-\nu, 1-\alpha, 1-\nu \\ 0, 1-\gamma, 1-\nu \end{matrix} \right) \\
&= [\Gamma(\nu)/t^\nu] {}_3F_2(\nu, \alpha, \nu; \gamma, \nu; t^{-1}) \\
&= [\Gamma(\nu)/t^\nu] {}_2F_1(\alpha, \nu; \gamma; t^{-1}) \quad [334]
\end{aligned}$$

The inverse Laplace transforms [226]-[229] are special cases of [330] and [334]. In the tables listed below, the eigenvalue spectra of the eigenfunctions of [281] for the different expansions and sign combinations are shown.

For the radial expansions, the numbering adopted is the same as was used in the Jaffé expansion of the original GSW-DE.

The parameter "k" refers to the expansion g_k used and the numbers in the tables below are identification tags for the eigenvalue spectra $\{A\}_i$, where $\{A\}_1$ is again the physically meaningful radial eigenvalue spectrum.

k	1	2	5	6	9	10	13	14
$p= p , R= R $	2,4	2,4	1,3	1,3	3,1	3,1	4,2	4,2
$p= p , R=- R $	1,3	1,3	2,4	2,4	4,2	4,2	3,1	3,1
$p=- p , R= R $	4,2	4,2	3,1	3,1	1,3	1,3	2,4	2,4
$p=- p , R=- R $	3,1	3,1	4,2	4,2	2,4	2,4	1,3	1,3

The numbers on the left of the commas apply to the infinite subblocks, where for the expansion index n we have $n \rightarrow -\infty$ and the number on the right holds for the infinite subblocks corresponding to $n \rightarrow +\infty$.

If $m \neq 0$ eight differently converging angular eigenvalue spectra are found. They interrelate as follows :

k	3	4	7	8	11	12	15	16
(i)	7,5	7,5	9,11	9,11	11,9	11,9	5,7	5,7
(ii)	8,6	8,6	10,12	10,12	12,10	12,10	6,8	6,8
(iii)	12,10	12,10	6,8	6,8	8,6	8,6	10,12	10,12
(iv)	11,9	11,9	5,7	5,7	7,5	7,5	9,11	9,11

For the Σ -states the following special situation arises :

$$\begin{aligned}
 m=0 : \quad \{A\}_5 &\equiv \{A\}_{12} \quad , \quad \{A\}_6 \equiv \{A\}_{11} \quad , \\
 \{A\}_7 &\equiv \{A\}_{10} \quad , \quad \{A\}_8 \equiv \{A\}_9
 \end{aligned}$$

In the table above the sign combinations were coded as shown in [73.5].

Jaffé Expansion of the Laplace Image

Since the inverse Laplace transform of the Jaffé expansion is

$$\mathcal{L}^{-1}\{(s+1)^{\alpha}((s-1)/(s+1))^{\nu}|t\} = [t^{(\alpha-1)} \exp(-t) \Phi(-\nu, \alpha; 2t)] \quad [335]$$

one would suspect that the same rate of convergence is obtained as for the expansions in confluent hypergeometric functions. It was indeed found that the previously found four radial eigenvalue spectra are generated. It appears that integral transform techniques provide no cure for the convergence problems encountered for the radial expansions.

For the different Laplace transformed GSW-DE's the algebraic eigenvalue problems associated with the Frobenius expansions in [256] interrelate as follows :

Expansion of [281] :

$\{A\}_k$	β_1^0	β_2	β_3^0	β_4
$p= p , R= R $	1	$2^{\dagger}$	$2^{\dagger}$	1
$p= p , R=- R $	2	$1^{\dagger}$	$1^{\dagger}$	2
$p=- p , R= R $	3	$4^{\dagger}$	$4^{\dagger}$	3
$p=- p , R=- R $	4	$3^{\dagger}$	$3^{\dagger}$	4

Expansion of [282] :

$\{A\}_k$	β_1°	β_2	β_3°	β_4
$p= p $, $R= R $	4	$3^\dagger$	$3^\dagger$	4
$p= p $, $R=- R $	3	$4^\dagger$	$4^\dagger$	3
$p=- p $, $R= R $	2	$1^\dagger$	$1^\dagger$	2
$p=- p $, $R=- R $	1	$2^\dagger$	$2^\dagger$	1

Expansion of [302] :

$\{A\}_k$	β_1°	β_2	β_3	β_4°
$p= p $, $R= R $	1	$2^\dagger$	1	$2^\dagger$
$p= p $, $R=- R $	2	$1^\dagger$	2	$1^\dagger$
$p=- p $, $R= R $	3	$4^\dagger$	3	$4^\dagger$
$p=- p $, $R=- R $	4	$3^\dagger$	4	$3^\dagger$

The $\{A\}_k$'s in the above three tables correspond to the $\{A\}_k$'s in the table following [269].

In the cases where a superscript " $^\circ$ " is indicated for the β 's the expansion index n has to be replaced by " $n-m$ " or its range has to be changed accordingly.

If $m=0$ the matrices for the Laplace image expansions are real symmetric. This is the case as well for [312] where an additional Laplace transform was taken. For this DE the truncated radial eigenvalue spectra are interrelated as follows :

Expansion of [312] :

$\{A\}_k$	β_1°	β_2	β_3°	β_4
$p= p $, $R= R $	3	$4^\dagger$	$3^\dagger$	4
$p= p $, $R=- R $	4	$3^\dagger$	$4^\dagger$	3
$p=- p $, $R= R $	1	$2^\dagger$	$1^\dagger$	2
$p=- p $, $R=- R $	2	$2^\dagger$	$2^\dagger$	1

However for $m \neq 0$ the off-diagonal elements for these are different from the ones of the Jaffé expansions of [281],[282] and [302]. In the cases where a "+" is indicated the corresponding matrices are adjoint to the ones where this "+" is missing.

The Laplace transform acts as the Rosetta stone to interconnect the expansions in confluent hypergeometric functions and Jaffé's Möbius transform. However no change in the convergence properties of the separation constant results from the use of Laplace transforms.

CHAPTER IV

In this chapter results of calculations on the particle in an electric dipole field of two point charges are given.

Rather frequently people consider free electrons in the company of polar molecules as electrons interacting with dipoles. Two examples of idealizations of physical situations resulting in the treatment of this system are : electron capture by rotational excitation of polar molecules ;⁽¹⁰⁾ theory of low-energy-electron scattering by polar molecules.⁽¹¹⁾

It was known previously that the binding energy of a particle in a dipole field becomes zero at some critical internuclear distance.⁽¹²⁾ In this chapter the "dipole theorem" is presented. It allows one to readily evaluate the critical distance for any combination of quantum numbers. Although no proof of this theorem acceptable in every respect will be shown, the correctness of this theorem is

considered to be established beyond any reasonable doubt. No extensive set of exact energies for this system existed previously. Results for ten states of the particle in a dipole field are presented here. As the critical points on the potential curves are approached numerical break-down of the radial expansion is encountered. The program performs a test for final convergence by extending the number of expansion terms considered and comparing with the previous result. Although the algorithms used in the computer program allow one to include essentially any number of terms in the expansions, it is believed that 45 expansion terms constitute an upper limit beyond which convergence tests such as the one mentioned become questionable.

The Particle in a Dipole Field

If $|z_1|=|z_2|$, we are dealing with a special case in the sense that for a given set of quantum numbers, the potential curve is related to the potential curve of the same energy state belonging to the pair of charges $|z_3|=|z_4|$ with

$$z_3 = \zeta z_1 \quad , \quad z_4 = \zeta z_2 \quad [336]$$

as shown by the following operations :

To obtain the energy belonging to z_1 and z_2 at $R_{1,2}$ take the energy belonging to z_3 and z_4 at $R_{3,4}$ where

$$R_{3,4} = R_{1,2}/\zeta \quad [337]$$

and divide this energy by the square of the scaling factor ζ

$$E_{1,2} = E_{3,4}/\zeta^2 \quad [338]$$

If $z_1=-z_2$ we have the situation discussed above.

The radial GSW-DE then becomes

$$\{(\lambda^2-1)D^2+2(m+1)\lambda D-(p\lambda)^2+m(m+1)-A_1\} L(\lambda) = 0 \quad [339]$$

Inspection of the above DE readily indicates that as $p \rightarrow 0$ the L's exhibit the following asymptotic behaviour :

$$L(\lambda) \sim (p\lambda)^{-(m+\frac{1}{2})} z_v(p\lambda) \quad , \quad v=(A_1+\frac{1}{4})^{\frac{1}{2}} \quad [340]$$

where the Z_u 's are modified Bessel functions if the limit is approached from the side $E_e > 0$.

If the substitution,

$$t = \lambda^2 \quad [341]$$

is made in [339] the following DE results

$$\{t(t-1)D^2 + [(m+(3/2))t - (1/2)]D - (p/2)^2 t + [(m(m+1) - A_1)/4]\} L(t) = 0 \quad [342]$$

Since one root of the indicial equation of [342] is " $\frac{1}{2}$ " a corresponding power can be factored out :

$$L(t) = \sqrt{t} h(t) \quad [343]$$

which gives

$$\{t(t-1)D^2 + [(m+(5/2))t - (3/2)]D - (p/2)^2 t + (1/2) + [(m(m+3) - A_1)/4]\} h(t) = 0 \quad [344]$$

Power series expansions of L and h such as

$$L(t) = \sum_{n=0}^{\infty} q_n^{(1)} t^n \quad [345]$$

$$L(t) = \sqrt{t} h(t) = \sqrt{t} \sum_{n=0}^{\infty} q_n^{(2)} t^n \quad [346]$$

give rise to the following pair of recurrence relations :

$$\begin{aligned} & -p^2 q_{n-1}^{(1)} + [4n(n+m+(1/2)) + m(m+1) - A_1] q_n^{(1)} \\ & -4[(n+(1/2))(n+1)] q_{n+1}^{(1)} = 0 \end{aligned} \quad [347]$$

$$\begin{aligned}
 & -p^2 q_{n-1}^{(2)} + [4n(n+m+(3/2)) + 2+m(m+3) - A_1] q_n^{(2)} \\
 & -4[(n+1)(n+(3/2))] q_{n+1}^{(2)} = 0
 \end{aligned} \tag{348}$$

As expected the eigenvalue spectra arising from [347] and [348] are the angular eigenvalue spectra for the bonding and antibonding states.

A rather interesting aspect of the use of Laplace transforms for the spheroidal wave functions is given by the following :

If one takes the Laplace transforms,

$$\mathcal{L}\{L(t-1) | s\} = \ell(s) \tag{349}$$

$$\mathcal{L}\{h(t-1) | s\} = j(s) \tag{350}$$

where the transforms satisfy,

$$\begin{aligned}
 & \{s^2 D^2 + [(p/2)^2 + ((5/2) - m)s - s^2] D + (m-1)s \\
 & + [(2+m(m-3) - p^2 - A_1)/4]\} \ell(s) = 0
 \end{aligned} \tag{351}$$

$$\begin{aligned}
 & \{s^2 D^2 + [(p/2)^2 + ((3/2) - m)s - s^2] D + (m-1)s \\
 & + [(m(m-3) - p^2 - A_1)/4]\} j(s) = 0
 \end{aligned} \tag{352}$$

then the power series expansions

$$\ell(s) = \sum_{n=-1}^{\infty} q_n^{(1)} s^n \tag{353}$$

$$j(s) = \sum_{n=-1}^{\infty} q_n^{(2)} s^n \tag{354}$$

are defined by the three-term recurrence relations

$$\begin{aligned}
 & 4[m-n] q_{n-1}^{(1)} + [4n(n-m+(3/2)) + 2+m(m-3) - p^2 - A_1] q_n^{(1)} \\
 & + [(n+1)p^2] q_{n+1}^{(1)} = 0
 \end{aligned} \tag{355}$$

$$4[m-n]q_{n-1}^{(2)} + [4n(n-m+(1/2)) + m(m-3) - p^2 - A_1]q_n^{(2)} + [(n+1)p^2]q_{n+1}^{(2)} = 0 \quad [356]$$

whose eigenvalue spectra are the ones for antibonding states if the Laplace preimages were bonding wave functions and vice versa.

This phenomenon can be explained by term-by-term inversion of the Laplace image,

$$L(\lambda) = \sum_{n=0}^{\infty} [q_n^{(1,2)} / \Gamma(n)] (\lambda^2 - 1)^n \quad [357]$$

and the relation of the Laplace transformed GSW-DE to its preimage for the case $Q=0$.

If $p=0$, [342] (also [344]!) becomes a hypergeometric DE. One solution is

$$L(t) = {}_2F_1((m+(1/2)+(A_1-(1/4))^{(1/2)})/2, \\ ((m+(1/2)-(A_1-(1/4))^{(1/2)})/2; \\ -(1/2); -t) \quad [358]$$

which is however unconditionally divergent if $m \geq 0$ on the boundary of the unit disk in the complex plane.

The limiting form of the radial wave functions as indicated in [340] suggests the use of a Neumann series expansion.

Substituting

$$x = p\lambda \quad [359]$$

in [339] gives

$$\{(x^2 - p^2)D^2 + 2(m+1)x D - x^2 + m(m+1) - A_1\} L(x) = 0 \quad [360]$$

If a power of x is factored out,

$$L(x) = x^{-(2m+1)/2} F_a(x) \quad [361]$$

[360] transforms into

$$\begin{aligned} & \{ (x^2 - p^2) D^2 + [x + ((2m+1)/x) p^2] D - x^2 - (1/4) - A_1 \\ & - (p/(2x))^2 (2m+1)(2m+3) \} F_a(x) = 0 \end{aligned} \quad [362]$$

then using the following Neumann expansions :

$$F_a(x) = \sum_n q_n^{(1)} I_n(x) \quad [363]$$

$$F_a(x) = \sum_n q_n^{(1)} K_n(x) \quad [364]$$

$$F_a(x) = \sum_n q_n^{(2)} J_n(ix) \quad [365]$$

$$F_a(x) = \sum_n q_n^{(2)} Y_n(ix) \quad [366]$$

and making use of the relations,

$$\{ x^2 D^2 + xD + (x^2 - n^2) \} Fb_n(x) = 0 \quad [367]$$

$$4D^2 Fb_n(x) = Fb_{n-2}(x) - 2Fb_n(x) + Fb_{n+2}(x) \quad [368]$$

$$\begin{aligned} (4/x) D Fb_n(x) &= (n-1)^{-1} Fb_{n-2}(x) - ((n+1)^{-1} - (n-1)^{-1}) \\ & Fb_n(x) - (n+1)^{-1} Fb_{n+2}(x) \end{aligned} \quad [369]$$

$$\begin{aligned} (4n/x^2) Fb_n(x) &= (n-1)^{-1} Fb_{n-2}(x) + ((n+1)^{-1} + (n-1)^{-1}) \\ & Fb_n(x) + (n+1)^{-1} Fb_{n+2}(x) \end{aligned} \quad [370]$$

where $Fb_n \equiv J_n$ or $Fb_n \equiv Y_n$

and

$$\{ x^2 D^2 + xD - (x^2 + n^2) \} Fc_n(x) = 0 \quad [371]$$

$$4D^2 Fc_n(x) = Fc_{n-2}(x) + 2Fc_n(x) + Fc_{n+2}(x) \quad [372]$$

$$\begin{aligned} (4/x) D Fc_n(x) &= (n-1)^{-1} Fc_{n-2}(x) + ((n+1)^{-1} - (n-1)^{-1}) \\ & Fc_n(x) - (n+1)^{-1} Fc_{n+2}(x) \end{aligned} \quad [373]$$

$$(4n/x^2)Fc_n(x) = (n-1)^{-1}Fc_{n-2}(x) - ((n+1)^{-1} + (n-1)^{-1})Fc_n(x) + (n+1)^{-1}Fc_{n+2}(x) \quad [374]$$

where $Fc_n \equiv I_n$ or $Fc_n \equiv K_n$,

one obtains the following three-term recurrence relations among the expansion coefficients in [363]-[366] :

$$\begin{aligned} & (p/2)^2 q_{n-2}^{(1,2)} [1 + [(m + (1/2))/(n-1)][2 + ((m + (3/2))/(n-2))]] \\ & - q_n^{(1,2)} [n^2 - (1/4) \pm (p/2)^2 [2 - (m + (1/2)) [2((n+1)^{-1} - (n-1)^{-1}) \\ & + (m + (3/2))((n(n+1))^{-1} + (n(n-1))^{-1})] - A_1] + (p/2)^2 q_{n+2}^{(1,2)} \\ & [1 - [(m + (1/2))/(n+1)][2 - ((m + (3/2))/(n+2))]] = 0 \end{aligned} \quad [375]$$

where the minus sign refers to the expansions in modified Bessel functions and the plus sign refers to expansions in Hankel or common Bessel functions.

If modified spherical Bessel functions are employed with

$$\begin{aligned} |n| & \geq m + \frac{1}{2} \quad \text{for bonding states} \\ |n| & \geq m + \frac{3}{2} \quad \text{for antibonding states} \end{aligned}$$

then the eigenvalue spectra for the angular expansions are obtained. The rate of convergence of these expansions is rather impressive. Expansions of the second lowest angular Σ -state with four and five expansion terms gave for the separation constant the number of significant figures shown in the following table :

p^2	0	5	10	15	20	25	30	35	40
4 terms >16		9	8	7	6	6	5	5	5
5 terms >16		13	11	10	9	8	7	7	7

From investigations which will be shown later in this section, evidence was obtained indicating that the radial expansions would be obtained if use could be made of Bessel functions of integer order. This can be done trivially if $p=0$. Furthermore such an expansion is possible if $m=-\frac{1}{2}$. The latter case, although physically meaningless is in a mathematical sense of distinguished importance, since for this case a substitution

$$\lambda = \cos(z) \quad [376]$$

in [339] gives a Hill-type DE known as Mathieu's DE. If $m \neq -\frac{1}{2}$ the expansion in Bessel functions of integer order cannot be obtained due to occurrences of inverse powers of the expansion index in the recurrence formula.

Later it will be shown that as $p \rightarrow 0$ the radial eigenvalue spectrum for the separation constant collapses into one infinitely degenerate eigenvalue, thus explaining the failure of the present approach.

If $p \rightarrow 0$ the limiting form of [340] will be

$$L(\lambda) \sim (p\lambda)^{-(m \pm \nu - \frac{1}{2})} \quad [377]$$

because the DE satisfied by $Z_\nu(p\lambda)$ becomes an equidimensional or Eulerian DE whose characteristic polynomial has the roots $\pm \nu$.

Therefore, if for $p=0$ we assume a trial function

$$\sqrt{N} L(\lambda) = \lambda^{-\varepsilon} \quad [378]$$

then for a proper exponent ε the correct eigenvalue spectrum should be obtained.

Taking the Rayleigh coefficient as a first approximation to A_1 using the trial function in [378] gives us

$$\begin{aligned} A_1^{-m(m+1)} &= \left[\frac{\int_0^\infty \lambda^{-\varepsilon} [(\lambda^2 - 1)D^2 + 2(m+1)\lambda D] \lambda^{-\varepsilon} d\lambda}{\int_0^\infty \lambda^{-2\varepsilon} d\lambda} \right] = \varepsilon \left[\left(\frac{(\varepsilon+1)}{(\varepsilon+\frac{1}{2})} \right) - \right. \\ &\quad \left. 2(m+1) \right] \quad , \quad \varepsilon > \frac{1}{2} \quad [379] \end{aligned}$$

The Rayleigh coefficient has a minimum if

$$\frac{\partial}{\partial \varepsilon} A_1 = \left(\frac{(\varepsilon+1)}{(\varepsilon+\frac{1}{2})} \right) - 2(m+1) - \left(\frac{\varepsilon}{(2(\varepsilon+\frac{1}{2}))^2} \right) = 0 \quad [380]$$

and if $m=0$ this is the case at

$$\varepsilon = 0 \quad , \quad A_1 = 0 \quad [381]$$

$$\varepsilon = -1 \quad , \quad A_1 = 2 \quad [382]$$

which however are located where the integrals in [379] do not converge.

If we use an additional term of a Frobenius expansion

$$L(\lambda) \sim (q_1 + q_2 \lambda^{-2}) \lambda^{-\epsilon} \quad [382.5]$$

the following Ritz-Galerkin eigenvalue problem arises :

$$\sum_{i=0}^1 \sum_{k=0}^1 c_i c_k \langle \lambda^{-(\epsilon+2i)} | \underline{S} | \lambda^{-(\epsilon+2k)} \rangle = 0 \quad [383]$$

with according to the Hylleraas-Undheim theorem improved eigenvalues. As before the differential operator of the spheroidal wave functions is written as $\underline{S}$. The expression in

[383] is equivalent to

$$\begin{aligned} -\det \begin{pmatrix} M_{11} - a_{11} A_1 & M_{12} - a_{12} A_1 \\ M_{21} - a_{21} A_1 & M_{22} - a_{22} A_1 \end{pmatrix} &= (a_{11} a_{22} - a_{12} a_{21}) A_1^2 \\ -(M_{11} a_{22} - M_{21} a_{12} - M_{12} a_{21} + M_{22} a_{11}) A_1 + M_{11} M_{22} - M_{12} M_{21} &= 0 \end{aligned} \quad [384]$$

where

$$\begin{aligned} M_{i+1, k+1} &= (\epsilon+2k) [[(\epsilon+2(k-m)-1) / (2(\epsilon+i+k)-1)] \\ &\quad - [(\epsilon+2k+1) / (2(\epsilon+i+k)+1)]] + [m(m+1) / (2(\epsilon+i+k)-1)] \\ &\quad \epsilon > \frac{1}{2} \end{aligned} \quad [385]$$

$$a_{i+1, k+1} = [2(\epsilon+i+k)-1]^{-1}, \quad \epsilon > \frac{1}{2} \quad [386]$$

The separation constant for a given ϵ is

$$\begin{aligned} A_1 &= [(M_{11} a_{22} - M_{21} a_{12} - M_{12} a_{21} + M_{22} a_{11}) \\ &\quad \pm [(M_{11} a_{22} - M_{21} a_{12} - M_{12} a_{21} + M_{22} a_{11})^2 - 4(a_{11} a_{22} - a_{12} a_{21}) \\ &\quad (M_{11} M_{22} - M_{12} M_{21})]^{1/2}] / [2(a_{11} a_{22} - a_{12} a_{21})] \end{aligned} \quad [387]$$

Now if for $p=0$ a power of λ is indeed an eigenfunction of [339], then for a unique ϵ there must be an eigenvalue

A_1 which is equal to the Rayleigh coefficient;
i.e. does not "improve" upon extending the basis
set. If a third term of the expansion is considered

$$L(\lambda) \sim (q_1 + (q_2/\lambda^2) + (q_3/\lambda^4))\lambda^{-\epsilon} \quad [388]$$

the following condition has to hold :

$$\det \begin{bmatrix} M_{11} - a_{11}A_1 & M_{12} - a_{12}A_1 & M_{13} - a_{13}A_1 \\ M_{21} - a_{21}A_1 & M_{22} - a_{22}A_1 & M_{23} - a_{23}A_1 \\ M_{31} - a_{31}A_1 & M_{32} - a_{32}A_1 & M_{33} - a_{33}A_1 \end{bmatrix} = 0 \quad [389]$$

which is equivalent to locating the roots of the
following characteristic polynomial :

$$\begin{aligned} & [a_{33}a_{21}a_{12} - a_{13}a_{21}a_{32} + a_{32}a_{23}a_{11} - a_{12}a_{23}a_{31} + a_{31}a_{22}a_{13} \\ & - a_{11}a_{22}a_{33}]A_1^3 + [a_{11}a_{22}M_{33} + a_{11}M_{22}a_{33} + M_{11}a_{22}a_{33} \\ & + a_{12}a_{23}M_{31} + a_{12}M_{23}a_{31} + M_{12}a_{23}a_{31} + a_{13}a_{21}M_{32} + a_{13}M_{21}a_{32} \\ & + M_{13}a_{21}a_{32} - a_{31}a_{22}M_{13} - a_{31}M_{22}a_{13} - M_{31}a_{22}a_{13} - a_{32}a_{23}M_{11} \\ & - a_{32}M_{23}a_{11} - M_{32}a_{23}a_{11} - a_{33}a_{21}M_{12} - a_{33}M_{21}a_{12} - M_{33}a_{21}a_{12}]A_1^2 \\ & - [M_{11}M_{22}a_{33} + M_{11}a_{22}M_{33} + a_{11}M_{22}M_{33} + M_{12}M_{23}a_{31} + M_{12}a_{23}M_{31} \\ & + a_{12}M_{23}M_{31} + M_{13}M_{21}a_{32} + M_{13}a_{21}M_{32} + a_{13}M_{21}M_{32} - M_{31}M_{22}a_{13} \\ & - M_{31}a_{22}M_{13} - a_{31}M_{22}M_{13} - M_{32}M_{23}a_{11} - M_{32}a_{23}M_{11} - a_{32}M_{23}M_{11} \\ & - M_{33}M_{21}a_{12} - M_{33}a_{21}M_{12} - a_{33}M_{21}M_{12}]A_1 + M_{11}M_{22}M_{33} + M_{12}M_{23}M_{31} \\ & + M_{13}M_{21}M_{32} - M_{31}M_{22}M_{13} - M_{32}M_{23}M_{11} - M_{33}M_{21}M_{12} = 0 \end{aligned} \quad [390]$$

Examining the graphs on the following pages one
finds that the lowest eigenvalues of the three
expansion sets cross at $\epsilon = \frac{1}{2}$. Although for this
characteristic exponent the wave function is not

Fig. IV

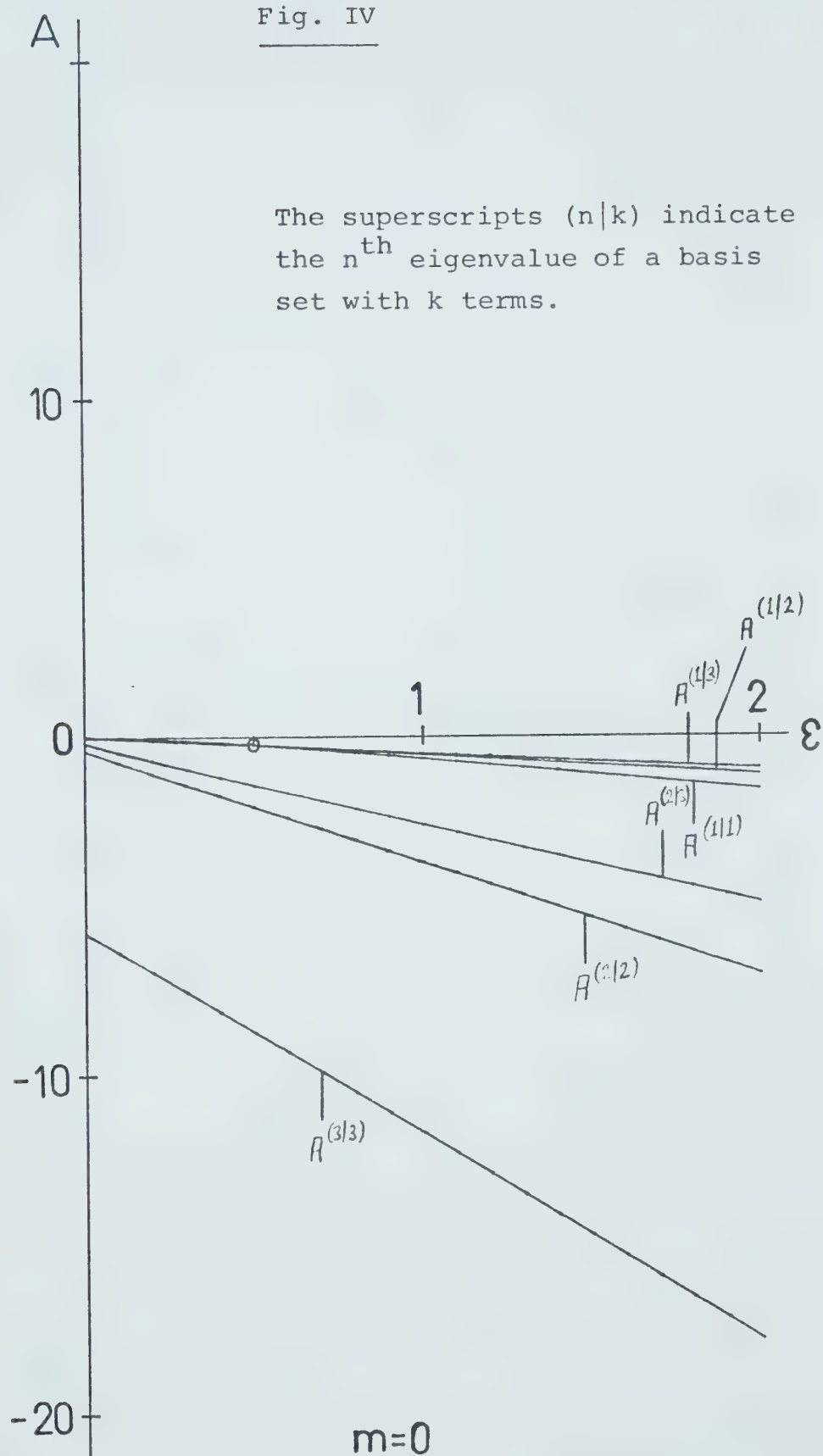


Fig. v

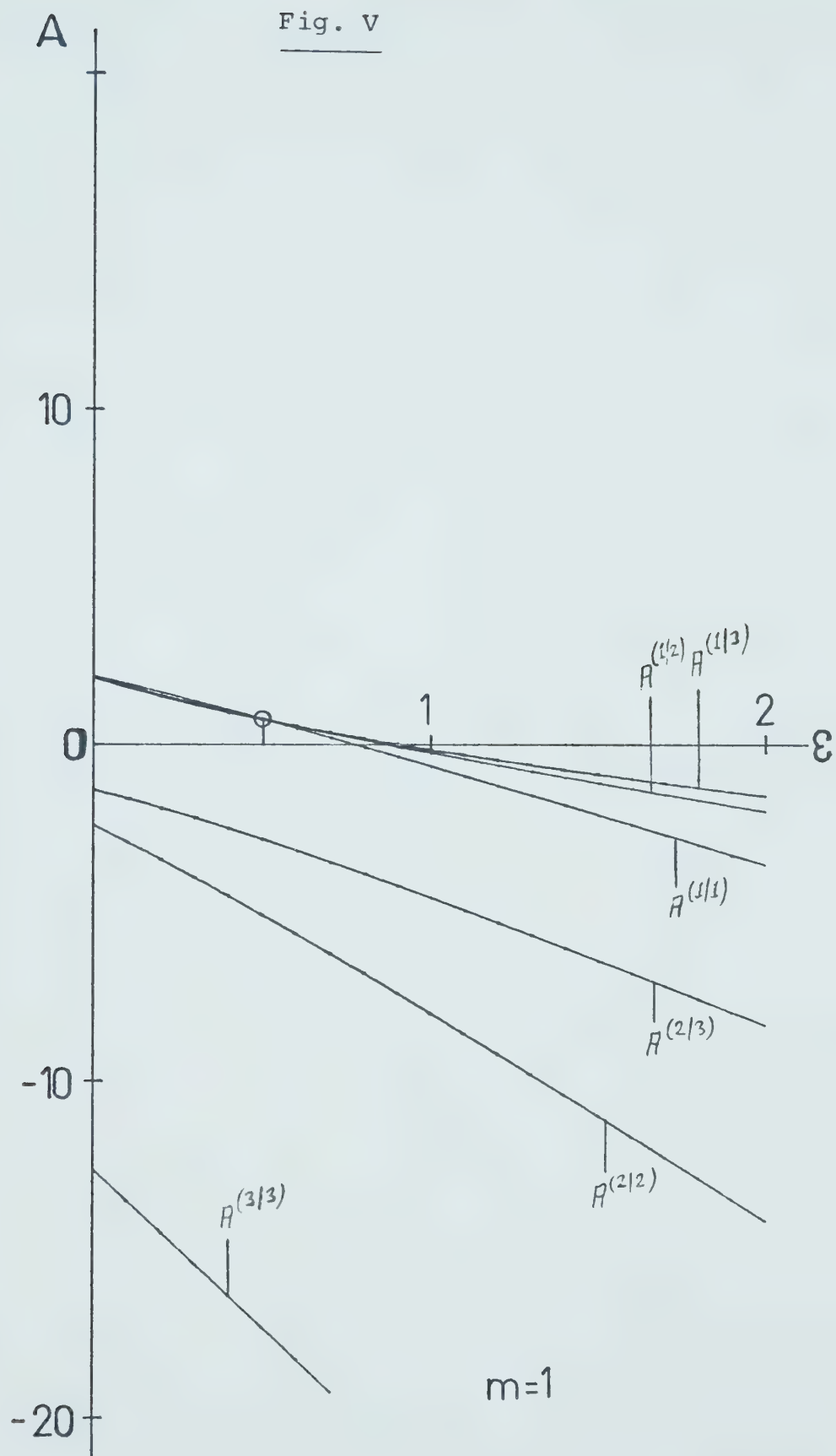


Fig. VI

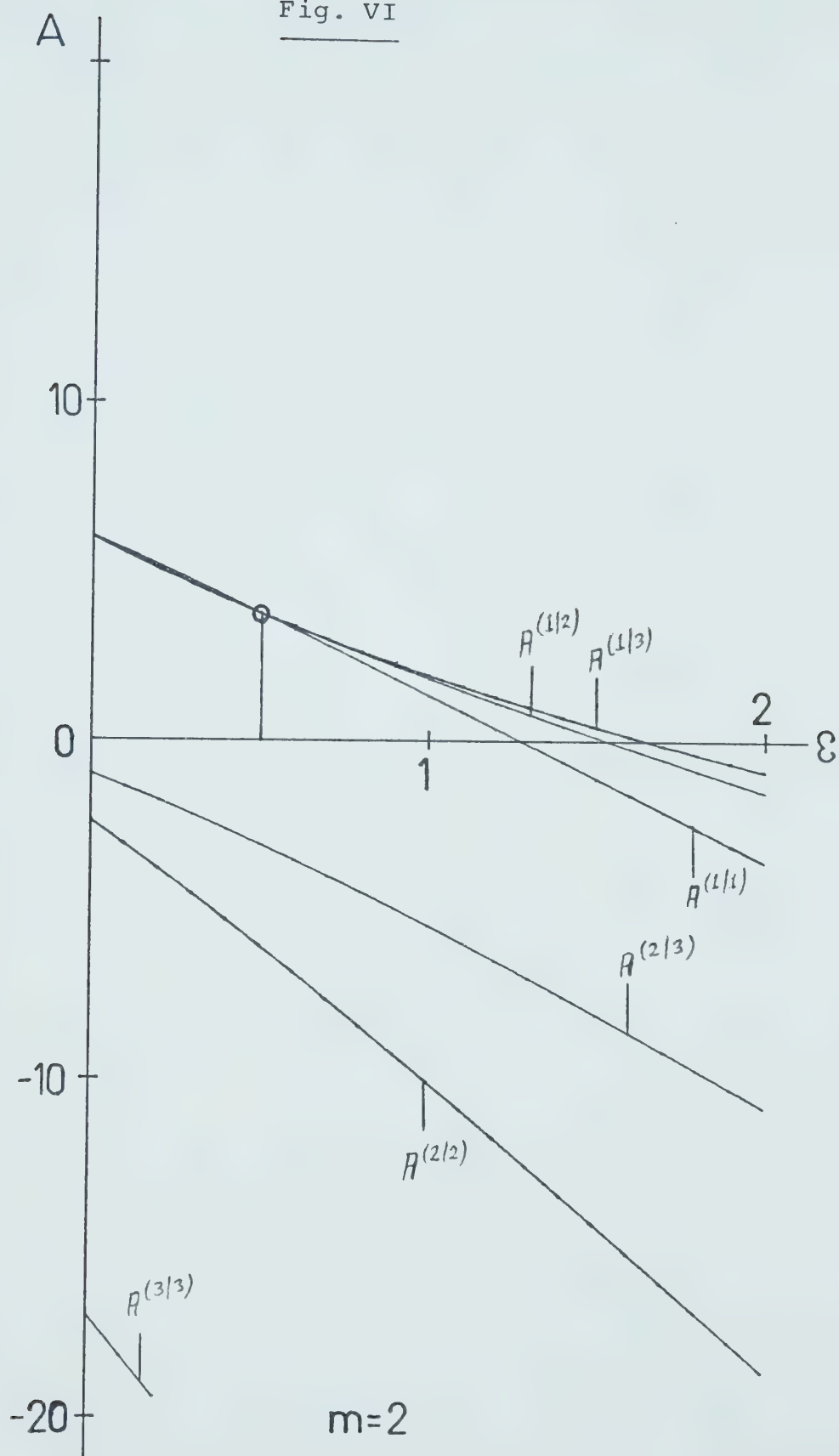
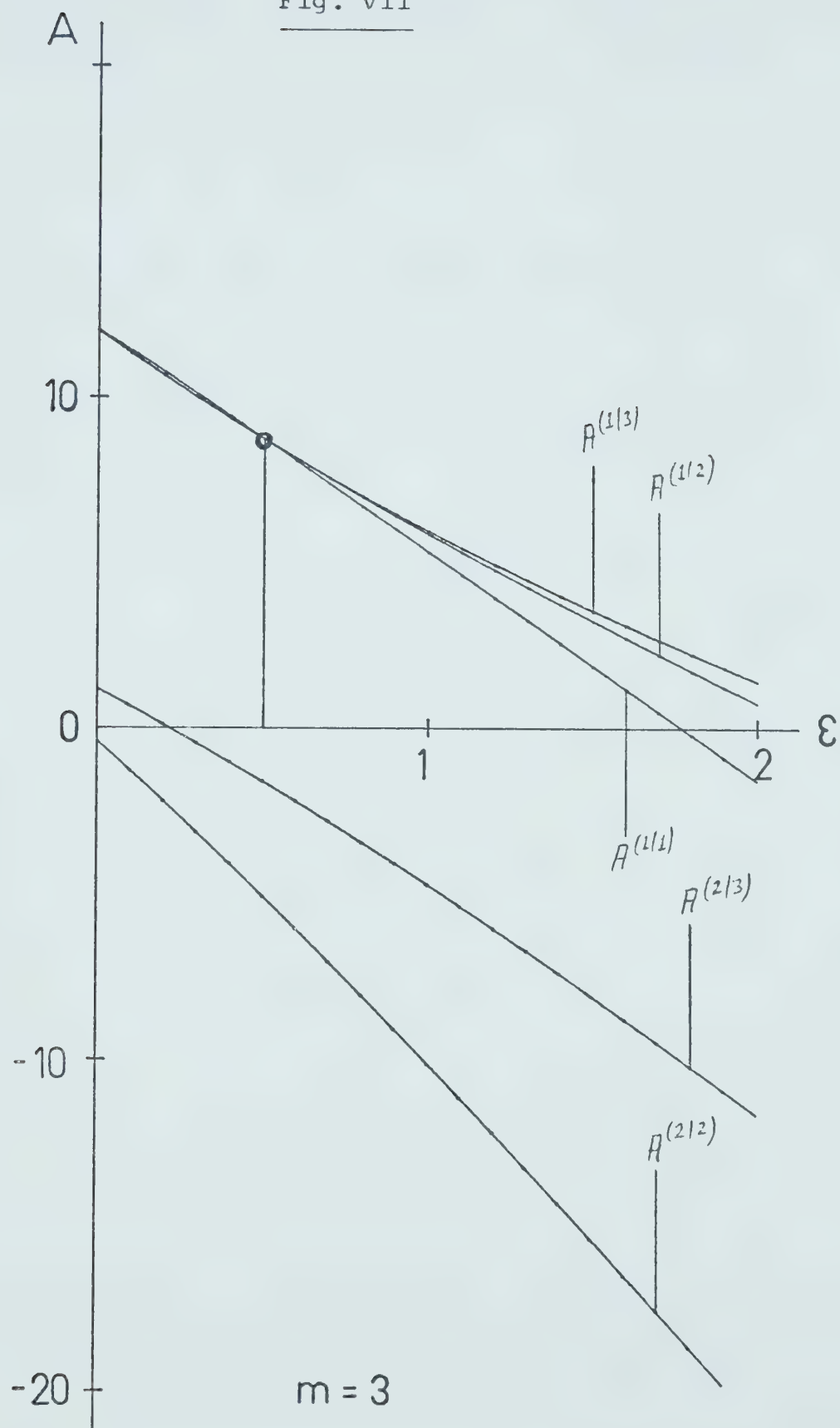


Fig. VII



square integrable, this value is still acceptable as a limit if some proper limiting process is used.

Substitution of $\epsilon = \frac{1}{2}$ in the expression for the Rayleigh coefficient gives

$$A_1 = m^2 - \frac{1}{4} \quad [391]$$

Another less laborious approach for finding the characteristic exponent ϵ is based on a theorem of upper and lower bounds of the eigenvalue established in 1929 by Kryloff and Bogoliubov⁽⁹⁾. We state this theorem as follows :

Having an eigenvalue problem

$$\underline{L}\{y(x)\} = \zeta g(x)y(x) \quad [392]$$

where $\underline{L}$ is a differential operator and $g(x) > 0$ and $y(x) \neq 0$ then for the quantities

$$\alpha = \int_a^b y \underline{L} y dx / \int_a^b g y^2 dx \quad [393]$$

$$\beta^2 = \int_a^b g^{-1} [\underline{L} y]^2 dx / \int_a^b g y^2 dx \quad [394]$$

the following holds :

$$\beta^2 \geq \alpha^2 \quad [395]$$

and between $\alpha - (\beta^2 - \alpha^2)^{1/2}$ and $\alpha + (\beta^2 - \alpha^2)^{1/2}$ at least one eigenvalue ζ is located.

The parameter α is the Rayleigh coefficient encountered previously. For β^2 , substitutions yield

$$\beta^2 = (2\varepsilon-1) \{ [\varepsilon(\varepsilon-2m-1)+m(m+1)]^2 / (2\varepsilon-1)-2\varepsilon(\varepsilon+1) \\ [\varepsilon(\varepsilon-2m-1)+m(m+1)] / (2\varepsilon+1) + \varepsilon^2(\varepsilon+1)^2 / (2\varepsilon+3) \} \\ \varepsilon > \frac{1}{2} \quad [396]$$

According to the theorem of Kryloff and Bogoliubov the interval in which at least one eigenvalue is located has zero width if $\alpha^2 = \beta^2$. In order to find the values for ε where this holds one would have to locate the roots of some rational function. However based on the previous investigation we are particularly interested in finding out what happens if $\varepsilon = \frac{1}{2}$. For this case $\alpha = \pm\beta$ becomes :

$$m^2 - \frac{1}{4} = \pm [m^2 - \frac{1}{4}] \quad [397]$$

where obviously the plus sign holds.

These investigations seem sufficient to establish the following theorem :

Theorem : "Dipole Theorem"

If $E_e = 0$ the separation constant eigenvalue spectrum of the radial expansion of the spheroidal wave DE becomes infinite-fold degenerate with

$$\{A_1\} \equiv m^2 - \frac{1}{4} \quad [398]$$

This means that the value $Q_a = R(Z_1 - Z_2)/2$ at which the binding energy of a particle in a dipole field of two point charges becomes zero is independent of the

radial quantum number. This result, although in a mathematical sense arising trivially, is rather unexpected in a physical sense because one would expect the binding energy of the particle to become zero if the Bohr radius of the hydrogenic system is appreciably penetrated by the additional charge.

The internuclear distance where the binding energy of an electron in a dipole field is zero is of considerable importance to radiation chemists working with negatively charged "heavy" particles. For a negatively charged "heavy" particle in dense matter, this distance gives us an indication with respect to the diameter of the tunnel along the trajectory of the particle in whose interior ionization of various "types" of electrons can occur. Turner and Fox⁽¹²⁾ calculated this distance for the ground state. The type of trial function used by these authors is very interesting.

The author calculated the value Q_a at $p=0$ for ten angular states where use was made of the previously stated "dipole theorem" and the angular expansion in ultraspherical polynomials. These data are presented on the next page. Turner and Fox indicate their result with six figures. However the last two of these are incorrect.

$ \ell, m\rangle$	Q_a (a.u.'s)	(*)
$ 0, 0\rangle$	0.639314877200	
$ 1, 0\rangle$	7.546955713228	
$ 2, 0\rangle$	21.300903309406	
$ 3, 0\rangle$	41.927307152002	
$ 1, 1\rangle$	2.692872106109	
$ 2, 1\rangle$	13.015258528456	
$ 3, 1\rangle$	30.206273990591	
$ 2, 2\rangle$	5.212816397259	
$ 3, 2\rangle$	19.067727486082	
$ 3, 3\rangle$	8.144777979975	

(*) 45 terms of the ultraspherical expansions were used with a subsequent increase of the basis set to 60 terms indicating 15 significant figures of the results.

If the charges are

$$|z_1| = |z_2| = 1 \quad [399]$$

i.e., a proton and a negatively charged meson,
 Q_a is the actual internuclear distance. Otherwise
 the formula

$$z_2 = -z_1 : \quad R = 2Q_a(z_1 - z_2) = Q_a/|z_1| \quad [400]$$

has to be used.

Notice how large some of the "distances of
 ionization" are. For the states $|n;3,0\rangle$ it is
 roughly 42 a.u.'s.

From $|n;3,2\rangle$ to $|n;3,0\rangle$ this distance increases
 from roughly 8 a.u.'s to roughly 42 a.u.'s which
 qualitatively would be expected since for large m 's
 the magnitude of the wave function in the region
 along the internuclear axis and hence in the
 neighbourhood of the negatively charged meson is
 small.

An extensive set of data was obtained by the
 author for the states $3 \geq n \geq l \geq m$. The first point in
 the corresponding ten tables was obtained by simply
 applying the "dipole theorem". We recall that this
 theorem was not established on a firm basis because
 the given eigenfunction was not square integrable
 over the physically meaningful domain. However the
 points derived from the "dipole theorem" fit nicely
 into the calculated energy curves.

$|1;0,0\rangle$

R	E	A	R	E	A
.6393	.0000	-.2500	3.8	-.2469	-5.3374
1.2	-.0077	-.7619	3.9	-.2527	-5.5820
1.3	-.0140	-.8723	4.0	-.2583	-5.8316
1.4	-.0220	-.9882	4.1	-.2637	-6.0862
1.5	-.0315	-1.1095	4.2	-.2688	-6.3457
1.6	-.0419	-1.2361	4.3	-.2738	-6.6103
1.7	-.0531	-1.3681	4.4	-.2785	-6.8798
1.8	-.0646	-1.5055	4.5	-.2831	-7.1543
1.9	-.0764	-1.6482	4.6	-.2875	-7.4338
2.0	-.0881	-1.7962	4.7	-.2917	-7.7182
2.1	-.0998	-1.9494	4.8	-.2958	-8.0076
2.2	-.1112	-2.1078	4.9	-.2998	-8.3020
2.3	-.1223	-2.2714	5.0	-.3035	-8.6014
2.4	-.1331	-2.4403	5.2	-.3107	-9.2150
2.5	-.1436	-2.6142	5.4	-.3174	-9.8485
2.6	-.1537	-2.7933	5.6	-.3237	-10.5019
2.7	-.1633	-2.9775	5.8	-.3296	-11.1752
2.8	-.1727	-3.1668	6.0	-.3351	-11.8683
2.9	-.1816	-3.3612	6.2	-.3402	-12.5813
3.0	-.1902	-3.5607	6.4	-.3451	-13.3142
3.1	-.1984	-3.7652	6.6	-.3497	-14.0671
3.2	-.2062	-3.9747	6.8	-.3540	-14.8398
3.3	-.2137	-4.1893	7.0	-.3581	-15.6324
3.4	-.2209	-4.4089	7.2	-.3520	-16.4449
3.5	-.2279	-4.6335	7.4	-.3656	-17.2773
3.6	-.2345	-4.8631	7.6	-.3691	-18.1296
3.7	-.2408	-5.0977	7.8	-.3724	-19.0019

R	E	A	R	E	A
8.0	-.3756	-19.8940	14.0	-.4286	-55.9345
8.4	-.3814	-21.7381	14.8	-.4325	-62.0977
8.8	-.3867	-23.6619	15.6	-.4359	-68.5806
9.2	-.3916	-25.6655	16.4	-.4391	-75.3833
9.6	-.3961	-27.7488	17.2	-.4419	-82.5057
10.0	-.4002	-29.9119	18.0	-.4445	-89.9480
10.4	-.4040	-32.1548	18.8	-.4468	-97.7101
10.8	-.4076	-34.4776	19.6	-.4490	-105.792
11.2	-.4109	-36.8801	20.4	-.4510	-114.194
11.6	-.4139	-39.3625	21.2	-.4528	-122.915
12.0	-.4168	-41.9248	22.0	-.4546	-131.957
12.4	-.4195	-44.5670	22.8	-.4561	-141.318
12.8	-.4220	-47.2890	23.6	-.4576	-151.000
13.2	-.4243	-50.0909	24.4	-.4590	-161.001
13.6	-.4265	-52.9728	25.2	-.4603	-171.322
			26.0	-.4615	-181.963
$ 2;0,0\rangle$			26.8	-.4627	-192.924
			27.6	-.4638	-204.205
			28.4	-.4648	-215.806
			29.2	-.4658	-227.727
			30.0	-.4667	-239.968
			∞	-.5000	----
			3.4	-.0067	-3.6574
			3.5	-.0074	-3.8071
			3.6	-.0081	-3.9581
			3.7	-.0088	-4.1104
			3.8	-.0095	-4.2638
			3.9	-.0103	-4.4185
			4.0	-.0110	-4.5744
.6393	.0000	-.2500			
2.8	-.0032	-2.7859			
2.9	-.0037	-2.9279			
3.0	-.0042	-3.0711			
3.1	-.0048	-3.2158			
3.2	-.0054	-3.3617			
3.3	-.0060	-3.5089			

R	E	A	R	E	A
4.1	-.0118	-4.7314	9.4	-.0488	-14.7604
4.2	-.0126	-4.8897	9.6	-.0498	-15.2049
4.3	-.0134	-5.0492	9.8	-.0509	-15.6542
4.4	-.0142	-5.2099	10.0	-.0519	-16.1084
4.5	-.0150	-5.3717	10.4	-.0538	-17.0314
4.6	-.0158	-5.5348	10.8	-.0556	-17.9739
4.7	-.0166	-5.6990	11.2	-.0574	-18.9360
4.8	-.0174	-5.8644	11.6	-.0591	-19.9175
4.9	-.0182	-6.0310	12.0	-.0607	-20.9187
5.0	-.0190	-6.1988	12.4	-.0622	-21.9394
5.2	-.0206	-6.5380	12.8	-.0636	-22.9797
5.4	-.0222	-6.8818	13.2	-.0651	-24.0397
5.6	-.0238	-7.2304	13.6	-.0664	-25.1194
5.8	-.0253	-7.5837	14.0	-.0677	-26.2187
6.0	-.0269	-7.9418	14.8	-.0701	-28.4764
6.2	-.0284	-8.3046	15.6	-.0723	-30.8130
6.4	-.0299	-8.6721	16.4	-.0744	-33.2286
6.6	-.0313	-9.0444	17.2	-.0763	-35.7233
6.8	-.0328	-9.4215	18.0	-.0781	-38.2971
7.0	-.0342	-9.8034	18.8	-.0798	-40.9501
7.2	-.0355	-10.1900	19.6	-.0813	-43.6824
7.4	-.0369	-10.5815	20.4	-.0828	-46.4941
7.6	-.0382	-10.9777	21.2	-.0841	-49.3851
7.8	-.0395	-11.3787	22.0	-.0854	-52.3556
8.0	-.0408	-11.7845	22.8	-.0866	-55.4056
8.2	-.0420	-12.1952	23.6	-.0877	-58.5350
8.4	-.0432	-12.6106	24.4	-.0888	-61.7441
8.6	-.0444	-13.0309	25.2	-.0898	-65.0327
8.8	-.0455	-13.4560	26.0	-.0908	-68.4009
9.0	-.0466	-13.8860	30.0	-.0949	-86.4370
9.2	-.0477	-14.3207	∞	-.1250	-----

$|2;1,0\rangle$

R	E	A	R	E	A
7.547	.00000	-.2500	12.4	-.03002	-6.2410
8.1	-.00016	-.7578	12.8	-.03292	-6.8814
8.2	-.00031	-.8534	13.0	-.03433	-7.2094
8.3	-.00052	-.9505	13.5	-.03771	-8.0517
8.4	-.00080	-1.0491	14.0	-.04090	-8.9257
8.5	-.00113	-1.1494	14.5	-.04392	-9.8314
8.6	-.00152	-1.2513	15.0	-.04676	-10.7685
8.7	-.00196	-1.3549	15.5	-.04943	-11.7369
8.8	-.00245	-1.4601	16.0	-.05196	-12.7364
8.9	-.00299	-1.5669	16.5	-.05434	-13.7670
9.0	-.00357	-1.6754	17.0	-.05658	-14.8287
9.1	-.00419	-1.7855	17.5	-.05870	-15.9214
9.2	-.00484	-1.8972	18.0	-.06071	-17.0450
9.3	-.00551	-2.0104	18.5	-.06260	-18.1995
9.4	-.00622	-2.1253	19.0	-.06440	-19.3850
9.5	-.00694	-2.2417	19.5	-.06610	-20.6014
9.6	-.00769	-2.3596	20.0	-.06771	-21.8487
9.7	-.00845	-2.4791	20.5	-.06925	-23.1268
9.8	-.00923	-2.6001	21.0	-.07070	-24.4359
9.9	-.01002	-2.7226	21.5	-.07209	-25.7759
10.0	-.01082	-2.8465	22.0	-.07341	-27.1468
10.2	-.01244	-3.0988	22.5	-.07467	-28.5486
10.4	-.01408	-3.3569	23.0	-.07587	-29.9813
10.6	-.01574	-3.6207	23.5	-.07702	-31.4449
10.8	-.01739	-3.8902	24.0	-.07812	-32.9395
11.0	-.01903	-4.1651	24.5	-.07917	-34.4651
11.2	-.02067	-4.4456	25.0	-.08017	-36.0216
11.4	-.02229	-4.7315	25.5	-.08113	-37.6090
11.6	-.02388	-5.0228	26.0	-.08206	-39.2275
11.8	-.02546	-5.3194	26.5	-.08294	-40.8769
12.0	-.02701	-5.6213	27.0	-.08379	-42.5573

R	E	A	R	E	A
27.5	-.08461	-44.2687	7.6	-.01832	-4.8982
28.0	-.08540	-46.0111	7.8	-.01988	-5.1931
28.5	-.08616	-47.7845	8.0	-.02145	-5.4930
29.0	-.08689	-49.5890	8.2	-.02299	-5.7980
29.5	-.08759	-51.4245	8.4	-.02453	-6.1081
30.0	-.08827	-53.2911	8.6	-.02604	-6.4232
∞	-.12500	----	8.8	-.02753	-6.7434
			9.0	-.02900	-7.0687
$ 2;1,1 >$			9.2	-.03045	-7.3990
2.693	.00000	.7500	9.4	-.03187	-7.7344
4.8	-.00069	-1.3056	9.6	-.03326	-8.0748
4.9	-.00094	-1.4169	9.8	-.03462	-8.4203
5.0	-.00124	-1.5294	10.0	-.03596	-8.7707
5.1	-.00159	-1.6432	10.4	-.03856	-9.4868
5.2	-.00197	-1.7581	10.8	-.04104	-10.2229
5.3	-.00240	-1.8744	11.2	-.04342	-10.9791
5.4	-.00286	-1.9919	11.6	-.04570	-11.7553
5.5	-.00336	-2.1106	12.0	-.04787	-12.5515
5.6	-.00390	-2.2306	12.4	-.04994	-13.3676
5.7	-.00446	-2.3519	12.8	-.05192	-14.2038
5.8	-.00506	-2.4744	13.2	-.05382	-15.0599
5.9	-.00568	-2.5982	13.6	-.05563	-15.9359
6.0	-.00632	-2.7233	14.0	-.05736	-16.8319
6.2	-.00767	-2.9773	14.8	-.06060	-18.6836
6.4	-.00909	-3.2364	15.6	-.06357	-20.6150
6.6	-.01056	-3.5006	16.4	-.06629	-22.6260
6.8	-.01207	-3.7699	17.2	-.06880	-24.7166
7.0	-.01361	-4.0443	18.0	-.07112	-26.8868
7.2	-.01517	-4.3239	18.8	-.07326	-29.1366
7.4	-.01674	-4.6085	19.6	-.07525	-31.4660
			20.4	-.07709	-33.8750
			21.2	-.07881	-36.3637

R	E	A
22.0	-.08041	-38.9320
22.8	-.08191	-41.5799
23.6	-.08332	-44.3075
24.4	-.08463	-47.1148
25.2	-.08587	-50.0017
26.0	-.08704	-52.9684
26.8	-.08814	-56.0149
27.6	-.08918	-59.1410
28.4	-.09016	-62.3469
29.2	-.09110	-65.6326
30.0	-.09198	-68.9981
∞	-.12500	----

 $|3;0,0\rangle$

.6393	.00000	-.2500
5.5	-.00194	-6.8451
6.0	-.00258	-7.6475
6.5	-.00328	-8.4627
7.0	-.00403	-9.2905
7.5	-.00481	-10.1307
8.0	-.00562	-10.9830
8.5	-.00644	-11.8475
9.0	-.00727	-12.7242
9.5	-.00810	-13.6130
10.0	-.00893	-14.5139
11.0	-.01056	-16.3527
12.0	-.01214	-18.2410
13.0	-.01366	-20.1791
14.0	-.01511	-22.1678

R	E	A
15.0	-.01650	-24.2073
16.0	-.01781	-26.2981
17.0	-.01905	-28.4406
18.0	-.02023	-30.6352
19.0	-.02134	-32.8821
20.0	-.02239	-35.1817
21.0	-.02339	-37.5341
22.0	-.02434	-39.9395
23.0	-.02523	-42.3983
24.0	-.02608	-44.9105
25.0	-.02689	-47.4762
26.0	-.02766	-50.0958
27.0	-.02839	-52.7692
28.0	-.02908	-55.4966
29.0	-.02974	-58.2781
30.0	-.03037	-61.1138
∞	-.05555	----

 $|3;1,0\rangle$

7.547	.00000	-.2500
10.0	-.00019	-2.6443
10.5	-.00040	-3.1769
11.0	-.00069	-3.7240
11.5	-.00106	-4.2855
12.0	-.00151	-4.8614
12.5	-.00204	-5.4518
13.0	-.00262	-6.0566
13.5	-.00325	-6.6758
14.0	-.00392	-7.3095

R	E	A
14.5	-.00462	-7.9576
15.0	-.00535	-8.6200
15.5	-.00609	-9.2968
16.0	-.00685	-9.9879
16.5	-.00761	-10.6933
17.0	-.00837	-11.4130
17.5	-.00913	-12.1469
18.0	-.00989	-12.8950
19.0	-.01138	-14.4339
20.0	-.01283	-16.0292
21.0	-.01423	-17.6809
22.0	-.01558	-19.3888
23.0	-.01687	-21.1528
24.0	-.01809	-22.9726
25.0	-.01927	-24.8483
26.0	-.02038	-26.7797
27.0	-.02144	-28.7667
28.0	-.02245	-30.8092
29.0	-.02341	-32.9073
30.0	-.02432	-35.0608
∞	-.05555	----

$|3;1,1 >$

2.693	.00000	.7500
7.5	-.00086	-4.5350
8.0	-.00129	-5.1852
8.5	-.00179	-5.8500
9.0	-.00237	-6.5289
9.5	-.00301	-7.2218

R	E	A
10.0	-.00369	-7.9285
10.5	-.00441	-8.6489
11.0	-.00515	-9.3830
11.5	-.00592	-10.1306
12.0	-.00669	-10.8918
12.5	-.00748	-11.6666
13.0	-.00826	-12.4549
13.5	-.00905	-13.2567
14.0	-.00983	-14.0721
14.5	-.01060	-14.9009
15.0	-.01136	-15.7434
16.0	-.01285	-17.4689
17.0	-.01428	-19.2486
18.0	-.01565	-21.0826
19.0	-.01696	-22.9710
20.0	-.01821	-24.9139
21.0	-.01939	-26.9112
22.0	-.02052	-28.9631
23.0	-.02159	-31.0696
24.0	-.02261	-33.2307
25.0	-.02357	-35.4466
26.0	-.02449	-37.7172
27.0	-.02536	-40.0426
28.0	-.02619	-42.4228
29.0	-.02697	-44.8579
30.0	-.02772	-47.3479
∞	-.05555	----

$|3;2,0\rangle$

R	E	A
21.30	.00000	-.2500
22.0	-.00006	-.8952
22.5	-.00031	-1.3837
23.0	-.00078	-1.8991
23.5	-.00139	-2.4395
24.0	-.00210	-3.0026
24.5	-.00289	-3.5864
25.0	-.00372	-4.1896
25.5	-.00459	-4.8111
26.0	-.00546	-5.4500
26.5	-.00634	-6.1057
27.0	-.00722	-6.7777
27.5	-.00810	-7.4656
28.0	-.00896	-8.1689
28.5	-.00981	-8.8874
29.0	-.01064	-9.6209
29.5	-.01145	-10.3691
30.0	-.01225	-11.1320
∞	-.05555	----

 $|3;2,1\rangle$

R	E	A
13.02	.00000	.7500
15.25	-.00008	-1.3385
15.5	-.00015	-1.5862
16.0	-.00039	-2.0926
16.5	-.00074	-2.6142
17.0	-.00120	-3.1515
17.5	-.00174	-3.7046
18.0	-.00236	-4.2735
19.0	-.00375	-5.4583
20.0	-.00527	-6.7051
21.0	-.00685	-8.0129
22.0	-.00844	-9.3806
23.0	-.01001	-10.8074
24.0	-.01154	-12.2927
25.0	-.01302	-13.8357
26.0	-.01445	-15.4360
27.0	-.01581	-17.0932
28.0	-.01711	-18.8070
29.0	-.01834	-20.5771
30.0	-.01952	-22.4032
∞	-.05555	----

$|3;2,2\rangle$

R	E	A	R	E	A
5.213	.00000	3.7500	18.0	-.00929	-11.0596
11.0	-.00018	-1.8475	19.0	-.01084	-12.6002
11.5	-.00043	-2.4152	20.0	-.01236	-14.1967
12.0	-.00079	-2.9964	21.0	-.01381	-15.8491
12.5	-.00125	-3.5913	22.0	-.01520	-17.5573
13.0	-.00180	-4.2000	23.0	-.01653	-19.3212
13.5	-.00241	-4.8227	24.0	-.01780	-21..407
14.0	-.00309	-5.4594	25.0	-.01900	-23.0157
14.5	-.00380	-6.1102	26.0	-.02015	-24.9463
15.0	-.00455	-6.7750	27.0	-.02123	-26.9322
15.5	-.00532	-7.4539	28.0	-.02227	-28.9736
16.0	-.00611	-8.1469	29.0	-.02324	-31.0703
16.5	-.00690	-8.8540	30.0	-.02418	-33.2224
17.0	-.00770	-9.5752	∞	-.05555	----
17.5	-.00850	-10.3104			

One would think that the energy of the system rapidly rises as soon as the negatively charged meson penetrates the Bohr radius of the electron. However the data above indicates that the energy rises gradually in such a process.

The ten dipole energy states which have been treated were identified as follows :

First a point on the $E_e(R)$ curve for the $H_2^+|n;\ell,m\rangle$ energy state close to the united atom limit was

evaluated. Then as points for larger internuclear distances were being calculated a small increment was simultaneously subtracted from Z_2 until $Z_2=-1$. This gave one single point for a large internuclear distance on the $E_e(R)$ curve of the $|n;\ell,m\rangle$ state of the dipole.

Starting with this point, additional points on the inner segment of the curve were obtained keeping $Z_2=-1$ and sweeping along the R -axis retaining the most recent values for p and A as initial approximations for the iterations.

CHAPTER V

In this chapter a radial expansion which becomes accurate as $R \rightarrow 0$ will be shown.

This expansion was tested in a fashion similar to the test procedures followed with the previously presented expansions. The expansion showed the expected behaviour in these tests. However it was not employed to calculate physical systems and there are some doubts that it can be efficiently used for numerical work unless an economical algorithm can be devised to evaluate two non-linear parameters in the expansion such that the convergence rate of the expansion is optimized.

Radial Expansion in Eigenfunctions for the

United Atom Limit

If $R \rightarrow 0$ the GSW-DE

$$\{(\lambda^2 - 1)D^2 + 2(m+1)\lambda D + m(m+1) - A\} L(\lambda) = 0 \quad [401]$$

for large λ 's becomes an Eulerian DE

$$\{\theta^2 + (2m+1)\theta + m(m+1) - A\} L(\theta) \sim 0$$

$$\theta \equiv \lambda(d/d\lambda) \quad , \quad |\lambda| \rightarrow \infty \quad [402]$$

whose char. polynomial has the pair of roots :

$$r_{1,2} = \pm \sqrt{A + \frac{1}{4}} - (m + \frac{1}{2}) \quad [403]$$

Based on the "dipole theorem" and the char. exponent ϵ which was determined in the previous section, the plus sign in [403] is the physically meaningful choice.

We proceed to factor out a power of λ using the GSW-DE with coefficients as specified in [212]-[216] :

$$\{x(x+4p)D^2 + [4p(m+1) + 2(m+1-2p)x - x^2]D + [(Q/p) - (m+1)]x + 2Q + (m-2p)(m+1) - p^2 - A\} Sw(x) = 0 \quad [404]$$

$$Sw(x) = x^a Sn(x) \quad [405]$$

which substituted into [404] gives :

$$\{[x(x+4p)D^2 + [4p(2a+m+1) + 2(a+m+1-2p)x - x^2]D + [(Q/p) - (a+m+1)]x + 2Q + (m-2p)(2a+m+1) + a(a+1) - p^2 - A] +$$

$$[4ap(m+a)]x^{-1}\} S_n(x) = 0 \quad [406]$$

where for $S_n(x)$ an expansion in confluent hypergeometric functions is desired

$$S_n(x) = \sum_n q_n \phi(n, c_1; x) \quad [407]$$

Substituting this expansion into [406] and making use of the relations :

$$\begin{aligned} x\phi(n, c_1; x) &= n\phi(n+1, c_1; x) + (c_1 - 2n)\phi(n, c_1; x) \\ &+ (n - c_1)\phi(n-1, c_1; x) \end{aligned} \quad [408]$$

$$xD\phi(n, c_1; x) = n[\phi(n+1, c_1; x) - \phi(n, c_1; x)] \quad [409]$$

gives the following expression :

$$\begin{aligned} \sum_n q_n \{ [n((2(a+m+1) - c_1) + (Q/p) + n - a - m - 1)] x\phi(n+1, c_1; x) \\ + [(c_1 - 2n)((Q/p) + n - a - m - 1) - n(2(a+m+1) - c_1) + 2Q + 4np \\ + (m - 2p)(2a + m + 1) + a(a + 1) - p^2 - A] x\phi(n, c_1; x) + [(n - c_1) \\ ((Q/p) + n - (a + m + 1))] x\phi(n-1, c_1; x) + [4p(2a + m + 1 - c_1)(xD) \\ + 4ap(m + a)] \phi(n, c_1; x) = 0 \end{aligned} \quad [410]$$

The following substitutions are convenient at this point :

$$Ga(n) = n(a + m + 1 + n - c_1 + (Q/p)) \quad [411]$$

$$\begin{aligned} Gb(n) &= (c_1 - 2n)((Q/p) + n - (a + m + 1)) - n(2(a + m + 1) \\ &- c_1) + 2Q + 4np + (m - 2p)(2a + m + 1) + a(a + 1) - p^2 - A \end{aligned} \quad [412]$$

$$Gc(n) = (n - c_1)((Q/p) + n - (a + m + 1)) \quad [413]$$

$$\eta = 4p(2a + m + 1 - c_1) \quad [414]$$

$$\nu = 4ap(m + a) \quad [415]$$

Then making additional use of the pair of relations

[408] and [409], the linear terms in [410] can be eliminated :

$$\begin{aligned} \sum_n q_n \{ (n+1)Ga(n)\phi(n+2, c_1; x) + [(c_1 - 2(n+1))Ga(n) + nGb(n) \\ + \eta n]\phi(n+1, c_1; x) + [(n+1-c_1)Ga(n) + (c_1 - 2n)Gb(n) + (n-1) \\ Gc(n) + (\eta - \nu n)]\phi(n, c_1; x) + [(n-c_1)Gb(n) + (c_1 - 2(n-1))Gc(n)] \\ \phi(n-1, c_1; x) + (n-1-c_1)Gc(n)\phi(n-2, c_1; x) \} = 0 \end{aligned} \quad [416]$$

Collecting equal expansion terms in [416] gives the following five-term recurrence relation among the expansion coefficients in [407] :

$$\begin{aligned} q_{n-2}[(n-1)Ga(n-2)] + q_{n-1}[\eta(n-1) + (c_1 - 2n)Ga(n-1) \\ + (n-1)Gb(n-1)] + q_n[(\eta - \nu n) + (n+1-c_1)Ga(n) + (c_1 - 2n)Gb(n) \\ + (n-1)Gc(n)] + q_{n+1}[(n+1-c_1)Gb(n+1) + (c_1 - 2n)Gc(n+1)] \\ + q_{n+2}[(n+1-c_1)Gc(n+2)] = 0 \end{aligned} \quad [417]$$

The choice of the parameters "a" and "c₁" is arbitrary. For the two limiting cases $R \rightarrow \infty$ and $R \rightarrow 0$ the fastest rates of convergence predictably occur if :

$$a = 0, \quad c_1 = m+1, \quad R \rightarrow \infty \quad [418]$$

$$a = \sqrt{A + \frac{1}{4}} - (m + \frac{1}{2}), \quad c_1 = \sqrt{4A+1} + 1, \quad R \rightarrow 0 \quad [419]$$

If these two parameters are chosen as in [418], approximating the radial Σ -ground-state with 7 or 21 terms, the following numbers of significant figures for the separation constant A are obtained :

	7 terms										21 terms									
p^2	.1 1.0										.1 1.0									
Q_r																				
.0	1	1	1	2	2	2	2	2	2	2	3	3	4	4	4	4	5	5	5	5
.1	1	1	2	2	2	2	2	2	2	2	3	3	4	4	4	5	5	5	5	5
.2	1	1	2	2	2	2	2	2	2	2	3	3	4	4	4	5	5	5	5	5
.3	2	2	2	2	2	2	2	2	2	2	4	4	4	4	4	5	5	5	5	5
.4	2	2	2	2	2	2	2	2	2	2	3	4	4	4	5	5	5	5	5	5
.5	2	1	2	2	2	2	2	2	2	2	4	3	5	5	5	5	5	5	5	6
.6	3	2	2	3	2	2	2	2	2	3	5	4	4	5	5	5	5	5	6	6
.7	3	2	2	2	3	3	3	3	3	3	5	4	4	4	6	5	5	6	6	6
.8	3	3	2	2	2	3	3	3	3	3	5	5	4	4	5	6	6	6	6	6
.9	4	4	2	2	2	2	3	4	3	3	6	6	5	5	4	5	6	7	6	6
1.0	4	3	3	2	2	2	2	3	3	-	7	6	5	5	5	5	5	6	6	-

As expected, the tables above show the same characteristics as the ones shown in Fig. III. To find the same number of significant figures for the separation constant as shown there, about twice as many expansion terms had to be included if use was made of the five-term recurrence relation [417], although the two expansions themselves are formally identical.

If the parameters "a" and " c_1 " are chosen as in [419], the number of significant figures will increase as $R \rightarrow 0$ (i. e. $p \rightarrow 0$).

This trend was empirically verified by data shown below :

p^2	.02	.03	.04	.05	.06	.07	.08	.09	0.1
Q_r									
0.6	5	4	4	3	3	3	2	2	2
0.7	4	3	2	2	2	1	0	2	2
0.8	6	5	4	4	3	3	3	3	2
0.9	7	6	5	4	4	3	3	3	3
1.0	8	6	5	5	4	4	4	3	3

where again the radial Σ -ground-state was approximated using 25 expansion terms in [407].

The confluent hypergeom. expansions with three-term recurrence relations do not converge satisfactorily if $R \sim 0$. As one can see from the table above, the drop-off in the number of significant figures with departure from the limiting case $p \sim 0$, especially for small R , is so drastic, that it appears doubtful that the entire range, in which the previous confluent hypergeom. radial expansions did not converge satisfactorily, could be covered. One major problem appears to be that for small R we have $\text{Im}(a) \neq 0$ which gives rise to an ugly singularity at the expansion centre :

$$x^a = x^{\text{Re}(a)} \{ \cos(\text{Im}(a) \ln(x)) + i \sin(\text{Im}(a) \ln(x)) \}$$

[420]

A scheme with promise for improvement makes use of the variational principle. Using for S_w the trial function

$$S_w(x) \sim x^\alpha \exp(-x/2) L_n^\beta(x) \quad [421]$$

where the Laguerre polynomials can be expressed

$$L_n^\beta(x) \equiv \Phi(-n, \beta+1; x) \quad [422]$$

For "A", the approximation by the Rayleigh coefficient is equivalent to :

$$\begin{aligned} A \sim & \int_0^\infty x^\alpha \exp(-x/2) L_n^\beta(x) [x(x+4p)D^2 + 2(m+1)(x+2p)D \\ & - (\tfrac{1}{4})x^2 + ((Q/p) - p)x + m(m+1) + 2Q - p^2] x^\alpha \exp(-x/2) L_n^\beta(x) dx \\ & / \int_0^\infty x^{2\alpha} \exp(-x) [L_n^\beta(x)]^2 dx \end{aligned} \quad [423]$$

Here use has been made of the differential operator satisfied by S_w as shown in [404].

Defining the quantities ,

$$\begin{aligned} M_{k+1, n+1} &= \int_0^\infty x^\alpha \exp(-x/2) L_k^\beta(x) [x(x+4p)D^2 + 2(m+1) \\ & (x+2p)D - (\tfrac{1}{4})x^2 + ((Q/p) - p)x + m(m+1) + 2Q - p^2] x^\alpha \exp(-x/2) \\ & L_n^\beta(x) dx \\ a_{k+1, n+1} &= \int_0^\infty x^{2\alpha} \exp(-x) L_k^\beta(x) L_n^\beta(x) dx \end{aligned} \quad [424]$$

higher orders of approximations of "A" can be obtained in the fashion indicated in [384] and [390].

Using the definition of the Gamma function

$$\int_0^\infty x^\alpha \exp(-x) dx = \Gamma(\alpha+1) \quad [425]$$

and writing the Laguerre polynomials as

$$L_n^\beta(x) = \sum_{j=0}^n (-1)^j \binom{n+\beta}{n-j} [x^j / (j)!], \quad [426]$$

the integrals in [421] and [422] can be evaluated :

$$M_{k+1,n+1} = \sum_{i=0}^k ((-1)^i / (i)!) \binom{k+\beta}{k-i} \sum_{j=0}^n ((-1)^j / (j)!) \binom{n+\beta}{n-j} \{ [(Q/p) - (j+\alpha+m+1)] \Gamma(i+j+2(\alpha+1)) + [(j+\alpha)(j+\alpha+1 + 2(m-2p)) + (m-2p)(m+1) + 2Q-p^2] \Gamma(i+j+2\alpha+1) + [4(j+\alpha)(j+\alpha+m) p] \Gamma(i+j+2\alpha) \} = 0 \quad [427]$$

$$a_{k+1,n+1} = \sum_{i=0}^k ((-1)^i / (i)!) \binom{k+\beta}{k-i} \sum_{j=0}^n ((-1)^j / (j)!) \binom{n+\beta}{n-j} \Gamma(i+j+2\alpha+1) \quad [428]$$

For the ground state [423] simply becomes :

$$A \sim M_{1,1} / a_{1,1} \quad [429]$$

For the expansion of a given GSW-DE the rate of convergence is considered close to its maximum if the Rayleigh coefficient in [423], or higher approximations, are optimized with respect to the non-linear parameters "a" and "c₁". (*)

Since the expansions for S_n become truncated for the two limiting cases R→∞ and R→0, if the conditions [418] and [419] are specified, the optimization suggested above should give for "a" and "c₁" the conditions [418] and [419] if the corresponding limit is approached. (**)

(*) where the restrictions Im(a)=0 and Im(c₁)=0 seem appropriate

(**) Notice that for the cases [418] and [419] the radial expansions become truncated indicating that for the n-th excited state the approximation "A_{n,n} M_{n,n} / a_{n,n}" is not suitable but instead higher orders of approximations of A (at least n-th order) seem to be required.

Although the algorithms required for the treatment above are straightforward, no actual numerical investigation of these speculations was undertaken.

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APPENDIX I

Computational Details,
Program Listing and
Sample Calculation for the HeH^{++}
 $|6;2,1\rangle$ State

Computational Details

For a given internuclear distance the separation constant and the energy are varied until they match for the radial and the angular expansion.

This is done as follows :

For a given R and $E_e(R)$ and an initial A formulating the algebraic eigenvalue problem

$$\det(\tilde{B}-A\tilde{I}) = 0 \quad [430]$$

corresponds to looking for the roots of the char. polynomial

$$p_n(A) = 0 \quad [431]$$

which can be done by Newton iterations

$$A_{i+1} = A_i + [p_n(A_i)/p'_n(A_i)] \quad [432]$$

To expand the characteristic polynomial of a tridiagonal matrix is easy enough. The expansion of the characteristic polynomial of a tridiagonal matrix was previously employed to show that the Hylleraas and the Jaffé expansions have identical rates of

convergence.

We can however equally well expand derivatives of the characteristic polynomial.

For the first derivative one obtains from [51]

$$p'_k(A) = (\alpha_k - A)p'_{k-1}(A) - \beta_k \gamma_k p'_{k-2}(A) - p_{k-1}(A) \quad [433]$$

and initially $p'_0(A)=0$ and $p'_1(A)=-1$.

For a given set of E and R the products $\beta_k \gamma_k$ can be evaluated, stored and recycled in successive Newton iterations.

Using Newton iterations has one outstanding advantage. It is the following : if one evaluates the characteristic polynomial of the algebraic eigenvalue problem there is great danger of overflow or underflow due to the limited range of magnitude allowed for real numbers by the available software of the machine.

However if the characteristic polynomial and its derivative are evaluated simultaneously one can easily implement a "trap" in the program which multiplies all recurrence terms by an integer power of 16 depending on which one of the two problems is building up. Then since only the ratio p_n/p'_n is of interest one does not have to keep track of all the multiplications performed to prevent "disaster". In practice those safety features apparently require more machine operations than the actual Newton iterations.

If for the angular and the radial expansions the roots of the characteristic polynomial are found one defines a function of p which is the difference between the pair of roots. If this function is zero the desired match between the two expansions has been achieved. The root of the latter function is located using the secant method. Since the Newton iterations are more rapidly convergent than the secant method, the total number of Newton iterations is restricted in the program to not more than six. These might not finally converge unless the secant method root search itself has advanced to its final converged state.

In order to test convergence in respect to the number of expansion terms considered, the program increases temporarily the demanded numbers of terms of both expansions by four and proceeds to calculate a pair of separation constants with the extended expansion set using the previous final converged value for p . If this pair of separation constants differs by more than a tolerated threshold supplied in the input, its value is printed at the right end of the corresponding output line.

Since the Newton iterations are very rapidly convergent, the algorithm described seems reasonably efficient in comparison with possible two-dimensional search schemes.

The computer program can be operated such that for a given energy state the separation constants and the energies are evaluated for many internuclear distances differing by a constant increment.

If this increment is comparatively large especially for heteronuclear species and large internuclear distances, there is great danger that the search jumps from one state to another or flips repeatedly between two states. This erratic behaviour can be considerably suppressed if one uses interpolation polynomials to predict the immediately following numbers of the search.

This is implemented in the computer program using a weighted second order least-squares polynomial. If previously at least four points on the $E_e(R)$ curve had converged, the new values for the separation constant and p are predicted giving the points increasing weight as one approaches the most recent point. The program uses the following :

$$w_1 = \frac{1}{2}, w_2 = 1/\sqrt{3}, w_3 = 1/\sqrt{2}, w_4 = 1 \quad [434]$$

A weighted least-square scheme for a second order polynomial is :

$$\begin{aligned} a_0 \sum_{i=1}^4 w_i + a_1 \sum_{i=1}^4 w_i x_i + a_2 \sum_{i=1}^4 w_i x_i^2 &= \sum_{i=1}^4 w_i y_i \\ a_0 \sum_{i=1}^4 w_i x_i + a_1 \sum_{i=1}^4 w_i x_i^2 + a_2 \sum_{i=1}^4 w_i x_i^3 &= \sum_{i=1}^4 w_i x_i y_i \\ a_0 \sum_{i=1}^4 w_i x_i^2 + a_1 \sum_{i=1}^4 w_i x_i^3 + a_2 \sum_{i=1}^4 w_i x_i^4 &= \sum_{i=1}^4 w_i x_i^2 y_i \end{aligned}$$

[435]

where x would be R and y either the energy (actually $p^2 = (\frac{1}{2})E_e(R)R^2$) or the separation constant A . Since for the points considered the internuclear distances differ by a constant increment we can make the following arbitrary choice :

$$x_1 = -1, x_2 = -\frac{1}{2}, x_3 = 0, x_4 = \frac{1}{2} \quad [436]$$

and the future point would be located at

$$x_{\text{new}} = 1 \quad [437]$$

Then

$$y_{\text{new}} = a_0 + a_1 x_{\text{new}} + a_2 x_{\text{new}}^2 = a_0 + a_1 + a_2 \quad [438]$$

is equivalent to :

$$y_{\text{new}} = 0.668151137905297y_1 - 1.004453413715892y_2 \\ - 0.995546586284109y_3 + 2.331848862094702y_4 \quad [439]$$

If less than four but at least two previous points were calculated and had converged, linear interpolation is used.

The computer program allows the matrix elements or the eigenvectors to be printed on a separate output unit. These features are however not at all exciting and for the actual use of the program at the beginning of the source listing one will find instructions for the preparation of input.

Furthermore a sample calculation is shown

following the program listing.

When using the program for numerical work one usually starts with a small internuclear distance for which the energy and the separation constant are approximately known by the "united-atom" limit and one chooses an increment for R which carries calculations into the region of interest. If one starts with too small an internuclear distance one occasionally encounters convergence problems for the radial expansion.

The computer program is rather fast. When for a great number of internuclear distances energy calculations were performed for the $\text{HeH}^{++}|6;2,1\rangle$ state, approximately 58 milliseconds were needed per point on the $E_e(R)$ curve. The machine employed was located at the University of Alberta which presently (1977) owns a hybrid consisting of IBM 370 software and an Amdahl 470 CPU.

Referring to the same calculation with the same machine the following histogram of distribution of CPU time among the main program and its subroutines was recorded :

MAIN	(Main program)	0.315%
FDIFF	(Function defined as the difference between the separation constants for the radial and the angular expansion for a given energy)	0.978%

DETA	(Calculation of the matrix elements for the homonuclear angular expansion)	0.000%
DETHET	(Calculation of the matrix elements for the heteronuclear angular expansion)	12.552%
DETR	(Calculation of the matrix elements for the radial expansion)	12.093%
DETRI	(Newton iterations)	73.520%
DETER	(Output of tridiagonal matrices)	0.000%
TRI	(Calculation and output of eigenvectors)	0.000%
INTPOL	(Control subroutine for interpolation)	0.030%
INTPL	(Interpolation subroutine)	0.071%
DSQRT	(Double precision IBM systems subroutine for the square root)	0.438%

The corresponding object program was prepared by the "FORTH" compiler specifying unrestricted optimization option.

The expansions used in the computer program are :

Homonuclear angular expansion :

(Generalized Legendre polynomials)
Formula [14]

Heteronuclear angular expansion :

(Ultraspherical polynomials)

Formula [38]

Radial expansion :

(Hylleraas expansion)

Formula [73].

The formulas indicated refer to the recurrence relations for the corresponding expansions.

The matrix elements for the homonuclear angular expansion are as indicated in [14] i.e. A_2 is divided by p^2 .


```

C ..... THIS PROGRAM PERFORMS CALCULATIONS FOR THE
C ... H2PL ... TWO-CENTER ONE-ELECTRON PROBLEM. ENERGIES ARE IN HARTREE'S
C ATOMIC UNITS.
C
C METHOD :
C PETER SENN, MASTERS THESIS (1977), UNIVERSITY OF ALBERTA,
C CANADA.
C
C INPUT :
C
C -----
C
C FIRST CARD :
C
C ILINE ..... THE OUTPUT ON OUTPUT UNIT "6" IS GROUPED IN
C BLOCKS WHICH ARE SEPARATED BY HORIZONTAL SPACINGS.
C "ILINE" DETERMINES THE SIZE OF THESE BLOCKS AND IS
C READ FROM INPUT UNIT "5" ONLY ONCE PER RUN OF THE
C PROGRAM. THE FORMAT USED IS "FORMAT (15)".
C
C -----
C
C LOGODD ..... FOR THE HOMONUCLEAR CASE IF "1" IS SPECIFIED
C FOR THIS LOGICAL CONSTANT CALCULATIONS WILL YIELD
C BONDING STATES. IF CORRESPONDINGLY "P" IS SPECIFIED
C FOR "LOGODD", ANTI-BONDING STATES WILL BE CALCULATED.
C
C N ..... THE DIMENSION OF THE MATRICES FOR
C CONSIDERED FOR THE ANGULAR EXPANSION. IF "N" IS
C ZERO OR NEGATIVE THE CORRESPONDING CARD IS THE
C LAST ONE. THE PROGRAM SETS N = |N|.
C
C NR ..... THE SAME AS "N" BUT REFERRED TO THE
C RADIAL EXPANSION.
C
C M ..... THE ANGULAR QUANTUM NUMBER AROUND THE
C INTERNUCLEAR AXIS.
C
C NRAD ..... THE NUMBER OF INTERNUCLEAR DISTANCES
C WITH AN INCREMENT "RDIFF" FOR WHICH ENERGY CALCULATIONS
C ARE DESIRED. IF "NRAD" IS ZERO OR NEGATIVE THE PAIR
C OF MATRICES WITH THE FINAL CONVERGED SEPARATION
C CONSTANTS WILL BE PRINTED ON OUTPUT UNIT "7" IN
C HEXADECIMAL CODE.
C THE DIMENSION OF THE OUTPUT MATRICES WILL BE N.
C THE PROGRAM SETS NRAD=|NRAD|.
C
C MAXIT ..... THE MAXIMUM NUMBER OF FUNCTION EVALUATIONS
C PERMITTED TO LOCATE THE ROOT WITHIN THE ERROR BOUND
C SPECIFIED IN "RDIFF".
C IF MAXIT IS ZERO OR NEGATIVE THE EIGENVECTORS FOR
C THE FINAL CONVERGED ENERGY AND SEPARATION CONSTANT
C WILL BE CALCULATED AND PRINTED ON OUTPUT UNIT "8"
C IN HEXADECIMAL CODE. THE PROGRAM SETS MAXIT = |MAXIT|.
C

```


E THE INITIAL CHOICE FOR THE ELECTRONIC ENERGY.
"E" HAS TO BE LESS THAN ZERO.

R INITIAL INTERNUCLEAR DISTANCE FOR WHICH THE
ENERGY AND THE SEPARATION CONSTANT WILL BE CALCULATED.
(SEE NRAD !!!)

RDIF INTERNUCLEAR DISTANCE INCREMENT. (SEE
NRAD !!!)

A INITIAL CHOICE FOR THE SEPARATION CONSTANT
FOR WHICH THE CALCULATIONS ARE EXPECTED TO CONVERGE
TO THE DESIRED ENERGY STATE.

CDIFS INCREMENT FOR "C" TO START THE ROOT
FINDING PROCEDURE USING A MODIFIED SECANT METHOD,
WHERE C = $-0.5 * E * R$.

CUTOFF TOLERATED ERROR OF THE FINAL CONVERGED
ENERGY.

THE NEXT CARD CONTAINS A LOGICAL CONSTANT AND THE
NUCLEAR CHARGES. THE LOGICAL CONSTANT IS "T" IF A
HOMONUCLEAR SPECIES IS BEING CALCULATED AND IT IS
SET "F" IF A HETERONUCLEAR SPECIES IS TREATED.

THE INPUT IS ORGANISED AS FOLLOWS :

LOGODD,N,NR,M,NRAD,MAXIT,E,R,EDIFF,A,CDIFF,CUTOFF

THIS DATA IS READ FROM INPUT UNIT "5" UNTIL "N" IS READ
IN AS ZERO OR NEGATIVE.

THE FORMAT USED IS :

FORMAT (L1,I4,I3,I2,2I5,5F10.0,E10.3/L1,F9.0,F10.0)

----- PETER SENN , UNIVERSITY OF ALBERTA -----

----- AUGUST 1977 -----

```

IMPLICIT REAL*8 (A-H,O-Z) , INTEGER*2 (I-N)
REAL*8 UP1(200),DIAG1(201),LOW1(200),
#      UP2(200),DIAG2(201),LOW2(200)
LOGICAL*1 LOGODD,LOGS,LOGU,LOGIT,LCGVEC,LTR,LSTOP,IFLAG,LZZ
COMMON /DIFF/ DIAG1,DIAG2,UP1,UP2,LOW1,LOW2,R,A1,A2,N,NR,LZZ
#/EVODD/LOGODD/COUNT/ISL/STOP/IFLAG/CHARGE/ZA,ZB
EQUIVALENCE (A1,A)
DATA IO,I1,T3,I4,I6,I7/0,1,3,4,6,7/,ONE,HALF/1.0D0,0.5D0/,LSTOP/.
#FALSE./,LTR/.TRUE./,CCUT/Z3A100000000000000/

```

A 58
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A 112
A 113
A 114

	READ (5,12) ILINE	A 115
	ISL = I0	A 116
	WRITE (6,14)	A 117
1	READ (5,13) LOGODD,N,NE,M,NRAD,MAXIT,E,R,FDIFF,A,CDIFS,CUTOFF,	A 118
	#LZZ,ZA,ZB	A 119
	CUTUFF = 0.125D0*CUTOFF	A 120
	RS = R	A 121
	SJ = 0.0D0	A 122
	CT = ONE+CUTOFF	A 123
	IF(N.LT.I1) LSTOP = .TRUE.	A 124
	IF(LSTOP) N = -N	A 125
	LOGVEC = .FALSE.	A 126
	IF(MAXIT.LT.J1) LOGVEC = .TRUE.	A 127
	IF(LOGVEC) MAXIT = -MAXIT	A 128
	LOGU = .TRUE.	A 129
	IF(NRAD.LT.I1) LOGU = .FALSE.	A 130
	IF(.NOT.LOGU) NRAD = -NRAD	A 131
	N1 = N-I1	A 132
	N4 = N+I4	A 133
	N4M1 = N+I3	A 134
	N1R = NR-I1	A 135
	N4R = NR+J4	A 136
	N4M1R = NR+I3	A 137
	A2 = A1	A 138
	C = -HALF*E*R*R	A 139
	DO 11 J=I1,NRAD	A 140
	SJ = SJ+ONE	A 141
	LOGS = .FALSE.	A 142
	LOGIT = LOGS	A 143
	YN = C	A 144
	FXN = FDIFF(XN,I7)	A 145
	CDIFF = 8.0D0*DABS(FXN)	A 146
	CDIFF = DMIN1(CDIFF,DABS(CDIFS))	A 147
	IF(CDIFF.LT.CCUT) CDIFF = CDIFS	A 148
	XNM1 = XN+CDIFF	A 149
	FXNM1 = FDIFF(XNM1,I7)	A 150
	FXNP1 = FDIFF(XN-CDIFF,I7)	A 151
	IF (DABS(FXNP1).GT.DABS(FXNM1)) GO TO 2	A 152
	FXNM1 = FXNP1	A 153
	XNM1 = XN-CDIFF	A 154
2	ISK = I0	A 155
	IFLAG = LOGS	A 156
	DO 7 JPK=I1,MAXIT	A 157
	IF (IFLAG) GO TO 1	A 158
3	IF ((XN.EQ.XNM1).OR.(FXN.EQ.FXNM1)) GO TO 4	A 159
	XNP1 = XN-FXN*((YN-XNM1)/(FXN-FXNM1))	A 160
	XNP1 = DMAX1(XNP1,CUTOFF)	A 161
	GO TO 5	A 162
4	XNM1 = XNM1*(CT)	A 163
	FXNM1 = FDIFF(XNM1,I7)	A 164
	ISK = ISK+I1	A 165
	IF (ISK.LE.MAXIT) GO TO 3	A 166
	LOGS = .TRUE.	A 167
	GO TO 8	A 168
5	FXNP1 = FDIFF(XNP1,I6)	A 169
	XDIFFS=XNP1-XN	A 170
	XNM1 = XN	A 171


```

FXNM1 = FXN
XN = XNP1
FXN = FXNP1
IF (LOGIT) GO TO 6
IF (DABS (FXNP1/A)+DABS ((XN-XNM1)/XN) .LT. CUTOFF) LOGIT = .TRUE.
GO TO 7
6 IF (DABS (FXNP1/A)+DABS ((XN-XNM1)/XN) .GT. CUTOFF) LOGIT = .FALSE.
IF (LOGIT) GO TO 6
7 IF (JNR.EQ.NAXIT) LOGS = .TRUE.
8 C = XN
IF (DABS (FXNM1) .LT. DABS (FXN)) C = XNM1
C CHECK ON FINAL CONVERGENCE.
IF (LZZ) CALL DETA (UP1,DIAG1,LOW1,C,M,N4)
IF (.NOT.LZZ) CALL DETHET (UP1,DIAG1,LOW1,A,C,E,N4)
CALL DETR (UP2,DIAG2,LOW2,R,C,M,N4R)
DO 9 JFK=11,16
IF (LZZ) A1 = -DETRI(UP1,DIAG1,LOW1,-A1/C,N4,N4M1,LTR)*C
IF (.NOT.LZZ) A1 = DETRI(UP1,DIAG1,LOW1,A1,N4,N4M1,LTR)
A2 = DETRI(UP2,DIAG2,LOW2,A2,N4R,N4M1R,LTR)
9 LTR = .FALSE.
LTR = .TRUE.
WN = DABS ((A1-A2)/A1)
IF (WN.GT.CUTOFF) LOGS = .TRUE.
ISL = ISL+11
IF (LOGS.OR.LOGU) GO TO 10
C OUTPUT OF THE MATRICES.
IF (LZZ) CALL DETA (UP1,DIAG1,LOW1,C,M,N)
IF (.NOT.LZZ) CALL DETHET (UP1,DIAG1,LOW1,R,C,M,N)
CALL DETR (UP2,DIAG2,LOW2,R,C,M,NR)
IF (LZZ) CALL DETER (UP1,DIAG1,LOW1,-A1/C,N,N1)
IF (.NOT.LZZ) CALL DETER (UP1,DIAG1,LOW1,A1,N,N1)
CALL DETER (UP2,DIAG2,LOW2,A2,NR,N1R)
10 AT = HALF*(A1+A2)
E = -(A1+C)/(1+A1)
ETOT = E+ONE/R
IF (.NOT.LOGS) WRITE (6,15) ISL,R,M,ZA,ZB,E,ETOT,AT,WN
IF (LOGS) WRITE (6,15) ISL,R,M,ZA,ZB,E,ETOT,AT,WN
DATA ICOUNT/0/
ICOUNT = ICOUNT+11
IF (((ICOUNT/ILINE)*ILINE).EQ.ICOUNT).AND.((J.NE.NRAD).OR.((.NOT.
#LSTOP))) WRITE (6,16)
IF (J.LT.NRAD) CALL INTPOL (A1,C,R*R,(R+RDIFF)**(2),J,LOGS)
A2 = A1
IF ((.NOT.LOGVEC).OR.LOGS) GO TO 11
C CALCULATION AND OUTPUT OF THE EXPANSION COEFFICIENTS.
IF (LZZ) CALL DETA (UP1,DIAG1,LOW1,C,M,N)
IF (LZZ) CALL TRI (LOW1,DIAG1,UP1,DIAG2,-A1/C,N)
IF (.NOT.LZZ) CALL DETHET (UP1,DIAG1,LOW1,R,C,M,1)
IF (.NOT.LZZ) CALL TRI (LOW1,DIAG1,UP1,DIAG2,A1,N)
CALL DETR (UP2,DIAG2,LOW2,R,C,M,NR)
CALL TRI (LOW2,DIAG2,UP2,DIAG1,A2,NR)
11 R = RS+SJ*RDIFF
IF (.NOT.ISTOP) GO TO 1
WRITE (6,17)
STOP

```


C		A 227
12	FORMAT (1F)	A 228
13	FORMAT (L1,I4,I3,I2,2I5,5F10.0,E10.3/L1,F9.0,F10.0)	A 229
14	FORMAT (1H1/1H-,40X,3HPHE,1X,10HTWO-CENTER,1X,12HONE-ELECTRON,1X, #7HPROBLEM/1H-,8X,1H+,5(19(1H-),1H+),/9X,1H ,5(19X,1H),/9X,1H ,2X, #10HINTERNUCL.,1X,5HDIST.,1X,1H ,3X,3HPHI,1X,7HQUANTUM,1X,1H#,3X, #1H ,3X,6HELECT.,1X,6HENERGY,3X,1H ,4X,5HTOTAL,1X,6HENERGY,3X,1H , #1X,10HSEPARATION,1X,6HCONST.,1X,1H ,/9X,1H ,5(19X,1H), #/9X,1H ,19X,1H ,3X,5HNUCL.,1X,7HCHARGES,3X,1H ,3(19X,1H),/9X, #1H ,5(19X,1H)/9X,1H+,5(19(1H-),1H+),/9X,1H ,5(19X,1H))	A 230 A 231 A 232 A 233 A 234 A 235
15	FORMAT (2X,I4,3X,1H ,F17.12,2X,1H ,I4,2F6.2,3X,1H ,3(F17.12,2X, #1H),2X,E10.3,2X,3H !!)	A 236 A 237
16	FORMAT (9X,1H ,5(19X,1H),/9X,1H+,5(19(1H-),1H+),/9X,1H ,5(19X,1H #))	A 238 A 239 A 240
17	FORMAT (9X,1H ,5(19X,1H),/9X,1H+,5(19(1H-),1H+),/1H) END	A 241 A 242 A 243
C		B 1
C		B 2
C	THIS FUNCTION EVALUATES THE DIFFERENCE BETWEEN THE	B 3
C	TWO EIGENVALUES OF INTEREST OF THE PAIR OF	B 4
C	TRIDIAGONAL MATRICES.	B 5
C		B 6
	REAL FUNCTION FDIFF*8 (C,NEND)	B 7
	IMPLICIT REAL*8 (A-H,O-Z), INTEGER*2 (I-N)	B 8
	REAL*8 UP1(200),DIAG1(201),LOW1(200),	B 9
	# UP2(200),DIAG2(201),LOW2(200)	B 10
	COMMON /DIFF/ DIAG1,DIAG2,UP1,UP2,LOW1,LOW2,R,A1,A2,M,N,NR,LZZ	B 11
	LOGICAL*1 LOGO,LOGA,LZZ	B 12
	EQUIVALENCE (A1PREV,A2PREV)	B 13
	DATA CPREV,RPREV/2*0.123459876D71/,I1/1/,PASS/1.0D-14/	B 14
	LOGA = .FALSE.	B 15
	LOGO = LOGA	B 16
	IF ((C.EQ.CPREV).AND.(R.EQ.RPREV)) GO TO 1	B 17
	LOGO = .TRUE.	B 18
	CPREV = C	B 19
	RPREV = R	B 20
	IF (LZZ) CALL DETA (UP1,DIAG1,LOW1,C,M,N)	B 21
	IF (.NOT.LZZ) CALL DETHET (UP1,DIAG1,LOW1,R,C,M,N)	B 22
	CALL DETR (UP2,DIAG2,LOW2,R,C,M,NR)	B 23
1	N1 = N-I1	B 24
	N1F = NR-I1	B 25
	IF (LZZ) A1 = -DETRI(UP1,DIAG1,LOW1,-A1/C,N,N1,LOGO)*C	B 26
	IF (.NOT.LZZ) A1 = DETRI(UP1,DIAG1,LOW1,A1,N,N1,LOGO)	B 27
	A2 = DETRI(UP2,DIAG2,LOW2,A2,NR,N1R,LOGO)	B 28
	A1PREV = A1	B 29
	LOGO = .FALSE.	B 30
	LOGA = LOGO	B 31
	DO 4 L=I1,NEND	B 32
	IF (LZZ) A1 = -DETRI(UP1,DIAG1,LOW1,-A1/C,N,N1,LOGO)*C	B 33
	IF (.NOT.LZZ) A1 = DETRI(UP1,DIAG1,LOW1,A1,N,N1,LOGO)	B 34
	IF (LOGA.AND.(DABS((A1-A1PREV)/A1).LT.PASS)) GO TO 3	B 35
	IF (DABS((A1-A1PREV)/A1).LT.PASS) LOGA = .TRUE.	B 36
2	A1PREV = A1	B 37
3	A2PREV = A2	B 38
	LOGA = .FALSE.	B 39
	DO 4 L=I1,NEND	B 40
	A2 = DETRI(UP2,DIAG2,LOW2,A2,NR,N1R,LOGO)	B 41
	IF (LOGA.AND.(DABS((A2-A2PREV)/A2).LT.PASS)) GO TO 5	B 42


```

C ----- D 1
C D 2
C THIS SUBROUTINE GENERATES THE MATRIX ELEMENTS D 3
C OF THE HETERONUCLEAR ANGULAR EXPANSIONS. D 4
C D 5
C SUBROUTINE DETHET(UPPER,DIAGON,LCWER,RST,P2,M,NDIM) D 6
C IMPLICIT REAL*8 (A-H,O-Z) , INTEGER*4 (I-N) D 7
C REAL*8 UPPER(2),DIAGON(2),LOWER(2) D 8
C INTEGER*2 M,NDIM D 9
C LOGICAL*1 LOGICO,IFLAG D 10
C COMMON /STOP/IFLAG/CHARGE/ZA,ZB D 11
C DATA I1/1/ D 12
C FUP(F1) = F1*(B+PT2*DFLOAT(N+M22)) D 13
C FLOW(F2) = F2*(B-DFLOAT(N11)*PT2) D 14
C LOGICO = .TRUE. D 15
C IF (P2.LT.0.000) GO TO 3 D 16
C R = RST*0.5D0*(ZA-ZB) D 17
C MM1 = M*(M+I1) D 18
C M2 = M+M D 19
C M21 = M2+I1 D 20
C M22 = M21+I1 D 21
C M23 = M22+I1 D 22
C M2M1 = M2-I1 D 23
C P = DSQRT(P2) D 24
C PT2 = P+P D 25
C B = R+R-P*DFLOAT(M22) D 26
C N = -I1 D 27
C N1 = 0 D 28
C GO TO 2 D 29
1 LOGICO = .FALSE. D 30
C UPPER(N1) = FUP(DFLOAT(N+M21)/DFLOAT(N2+M23)) D 31
C DIAGON(N1) = DFLOAT(MM1+N*(N+M21))-P2 D 32
2 N11 = N D 33
C N = N1 D 34
C N1 = N1+I1 D 35
C N2 = N+N D 36
C IF (LOGICO) GO TO 1 D 37
C DIAGON(N1) = DFLOAT(MM1+N*(N+M21))-P2 D 38
C LOWER(N) = FLOW(DFLOAT(N)/DFLOAT(N2+M2M1)) D 39
C IF (N.EQ.NDIM) GO TO 4 D 40
C UPPER(N1) = FUP(DFLOAT(N+M21)/DFLOAT(N2+M23)) D 41
C GO TO 2 D 42
3 WRITE (6,5) D 43
C IFLAG = LOGICO D 44
4 RETURN D 45
C D 46
5 FORMAT (1H-,9X,6HSEARCH,1X,5HAAREA,1X,3HFOR,8HPOSITIVE,1X, D 47
C #8HENERGIES,1X,9HSPECIFIED,1X,3H!!!,/1H0) D 48
C END D 49
C D 50

```



```

C ----- F 1
C F 2
C THIS SUBROUTINE GENERATES THE MATRIX E 3
C ELEMENTS OF THE RADIAL EXPANSION. E 4
C E 5
SUBROUTINE DETR (UPPER,DIAGON,LOWER,RST,C,M,NDIM) L 6
IMPLICIT REAL*8 (A-H,O-Z) , INTEGER*4 (I-N) E 7
REAL*8 DIAGON(2),UPPER(2),LOWER(2) F 8
INTEGER*2 M,NDIM F 9
LOGICAL*1 LOGICO,IFLAG F 10
COMMON /STOP/IFLAG/CHARGE/ZA,ZB F 11
DATA I1/1/ E 12
FUP(NM) = DFLOAT(NM)-DFLOAT(N)*SQRTRC E 13
FDIAG(NM1) = DFLOAT(NM+N1)*(SQRTRC-DFLOAT(N))+(REC+DFLOAT(NM1)- E 14
#SQC*DFLOAT(2*(NM+N1))) E 15
FLOM(N1N1M) = DFLOAT(N1N1M)-DFLOAT(N1-M)*SQRTRC L 16
LOGICO = .TRUE. F 17
IF (C.LT.0.0D0) GO TO 4 L 18
R = RST*0.5D0*(ZA+ZB) F 19
SQC = DSQRT(C) F 20
SQTRC = R/SQC F 21
REC = R+R-C F 22
M1 = M+I1 E 23
N = M1 E 24
LOC = I1 E 25
GO TO 3 E 26
1 LOGICO = .FALSE. E 27
UPPER(LOC) = FUP(N*NM) E 28
DIAGON(LOC) = FDIAG(N1*M1) E 29
2 N = N+I1 E 30
LOC = LOC+I1 E 31
3 N1 = N-I1 E 32
NM = N-I1 E 33
IF (LOGICO) GO TO 1 E 34
DIAGON(LOC) = FDIAG(N1*M1) E 35
LOWER(LOC-I1) = FLOM(N1*(N1-M)) E 36
IF (LOC.EQ.1D1D) GO TO 5 F 37
UPPER(LOC) = FUP(N*NM) E 38
GO TO 2 E 39
4 WRITE (6,6) E 40
IFLAG = LOGICO E 41
5 RETURN E 42
C E 43
6 FORMAT (1H-,9X,6HSEARCH,1X,5HAAREA,1X,3HFOR,1X,8HPOSITIVE,1X, E 44
#AND,1X,8HNEG,1X,8HPOSITIVE,1X,3HFOR,1X,8HPOSITIVE,1X, E 45
END E 46
C E 47

```



```

C ----- F 1
C F 2
C THIS FUNCTION PERFORMS ONE NEWTON ITERATION TO F 3
C FIND ONE ROOT OF THE EQUATION DET(A)=0 , WHERE F 4
C "A" IS A TRIDIAGONAL MATRIX. F 5
C F 6
C REAL FUNCTION DETRI*8 (B,A,C,Z,N,N1,LOGIC) F 7
C IMPLICIT REAL*8 (A-H,O-Z) , INTEGER*2 (I-N) F 8
C REAL*8 A(2),B(2),G(2),LOWLIM F 9
C LOGICAL*1 LOGIC F 10
C DATA IONE/1/,CUT/Z3310000000000000/,UPLIM/Z5510000000000000/, F 11
C #LOWLIM/Z2D1000000000000000/,FACTOR/Z3710000000000000/ F 12
C IF (.NOT.LOGIC) GO TO 2 F 13
C DO 1 J=IONE,N1 F 14
C 1 B(J) = B(J)*G(J) F 15
C 2 PR2 = 1.000 F 16
C DETRI = PR2 F 17
C DERIVA = PR2 F 18
C PR1 = A(IONE)-Z F 19
C PRDOT1 = -PR2 F 20
C PRDOT2 = 0.000 F 21
C IF (N.EQ.IONE) GO TO 9 F 22
C J = IONE F 23
C 3 J = J+1ONF F 24
C A0 = A(J)-Z F 25
C A1 = B(J-IONE) F 26
C OVERFLOW PROTECTION SECTION : F 27
C IF ((DABS(DETRI)+DABS(DERIVA)).LT.UPLIM) GO TO 4 F 28
C IF ((DABS(PR1).LT.LOWLIM).OR.(DABS(PR2).LT.LOWLIM).OR. F 29
C # (DABS(PRDOT1).LT.LOWLIM).OR.(DABS(PRDOT2).LT.LOWLIM)) GO TO 4 F 30
C PR1 = PR1*FACTOR F 31
C PR2 = PR2*FACTOR F 32
C PRDOT1 = PRDOT1*FACTOR F 33
C PRDOT2 = PRDOT2*FACTOR F 34
C GO TO 7 F 35
C 4 IF ((DABS(DETRI).GT.LOWLIM).AND.(DABS(DERIVA).GT.LOWLIM)) GO TO 7 F 36
C IF ((DABS(PR1).GT.UPLIM).OR.(DABS(PR2).GT.UPLIM).OR. F 37
C # (DABS(PRDOT1).GT.UPLIM).OR.(DABS(PRDOT2).GT.UPLIM)) GO TO 7 F 38
C PR1 = PR1/FACTOR F 39
C PR2 = PR2/FACTOR F 40
C PRDOT1 = PRDOT1/FACTOR F 41
C PRDOT2 = PRDOT2/FACTOR F 42
C 7 DETRI = A0*PR1-A1*PR2 F 43
C DERIVA = A0*PRDOT1-A1*PRDOT2-PR1 F 44
C IF ((J.EQ.N).OR.(DABS(Z*DERIVA)/DET F 45
C PR2 = PR1 F 46
C PRDOT2 = PRDOT1 F 47
C PR1 = DETRI F 48
C PRDOT1 = DERIVA F 49
C GO TO 3 F 50
C 8 DETRI = Z-DETRI/DERIVA F 51
C RETURN F 52
C 9 DETRI = PR1 F 53
C DERIVA = PRDOT1 F 54
C GO TO 8 F 55
C END F 56
C F 57

```


C	-----	G	1
C		G	2
C	THIS SUBROUTINE PRINTS A TRIDIAGONAL MATRIX	G	3
C	IN ITS HEXADECIMAL FORM ON I/O UNIT "7".	G	4
C		G	5
	SUBROUTINE DETER (A,D,E,EIG,N,N1)	G	6
	IMPLICIT REAL*8 (A-H,O-Z) , INTEGER*2 (I-N)	G	7
	REAL*8 A(2),D(2),B(2)	G	8
	COMMON /COUNT/ ISL	G	9
	DATA I1/1/	G	10
	WRITE (7,4) ISL	G	11
	WRITE (7,2) FIG	G	12
	DO 1 J=I1,N1	G	13
1	WRITE (7,2) A(J),D(J),E(J)	G	14
	WRITE (7,3) D(N)	G	15
	RETURN	G	16
C		G	17
2	FORMAT (1X,3216)	G	18
3	FORMAT (17X,216)	G	19
4	FORMAT (1X,15)	G	20
	END	G	21
C	-----	G	22
C		E	1
C		E	2
C	THIS SUBROUTINE EVALUATES THE EIGENVECTOR OF A	E	3
C	TRIDIAGONAL MATRIX BELONGING TO A SPECIFIED	E	4
C	EIGENVALUE. THEN THE EIGENVECTOR IS WRITTEN	E	5
C	ON THE I/O UNIT "8" IN HEXADECIMAL CODE.	E	6
C		E	7
	SUBROUTINE EIV (SUB,DIAG,EIG,N,N1,IC)	E	8
	IMPLICIT REAL*8 (A-H,O-Z) , INTEGER*2 (I-N)	E	9
	REAL*8 SUB(2),DIAG(2),SUP(1),B(2)	E	10
	LOGICAL*1 LULU	E	11
	COMMON /COUNT/ ISL	E	12
	DATA I1,I2/1,2/,ONE/1.0D0/	E	13
	LULU = .FALSE.	E	14
	DO 1 J=I1,N	E	15
1	DIAG(J) = DIAG(J)-EIG	E	16
	B(I1) = ONE	E	17
	IF (N.IQ.I1) GO TO 9	E	18
	DO 2 K=I2,N	E	19
	IK = K-I1	E	20
	RATIO = -SUB(IK)/DIAG(IK)	E	21
2	DIAG(K) = DIAG(K)+RATIO*SUP(IK)	E	22
	DO 3 IK=I2,N	E	23
	K = IK-I1	E	24
3	B(IK) = -(DIAG(K)*B(K))/SUP(K)	E	25

	DO 6 K=I2,N	H	26
	NUMBER = K	H	27
	IF (NUMBER.EQ.N) GO TO 6	H	28
	IF (DABS(B(K+1))-DABS(B(K))) 4,4,5	H	29
4	LULU = .TRUE.	H	30
	GO TO 6	H	31
5	IF (LULU) GO TO 7	H	32
6	B(I1) = B(I1)+B(K)*B(K)	H	33
7	B(I1) = ONE/DSQRT(B(I1))	H	34
	DO 8 K=I2,NUMBER	H	35
8	B(K) = B(K)*B(I1)	H	36
9	IF (N.EQ.I1) NUMBER = I1	H	37
	WRITE (8,12) ISL,NUMBER	H	38
	DO 10 K=I1,NUMBER	H	39
10	WRITE (8,11) B(K)	H	40
	RETURN	H	41
C		H	42
11	FORMAT (1X,Z16)	H	43
12	FORMAT (1X,2T5)	H	44
	END	H	45
C		H	46
C	-----	I	1
C		I	2
C	SUBROUTINE TO CONTROL INTERPOLATION SECTION.	I	3
C		I	4
C	SUBROUTINE INTPOL (A,C,PR,RD,J,LOGS)	I	5
	IMPLICIT REAL*8 (A-H,O-Z) , INTEGER*2 (I-N)	I	6
	REAL*8 APREV(4),CPREV(4)	I	7
	LOGICAL*1 LOGS,LG,LAY	I	8
	DATA JS,I1,I1,TS/ 10,1,2/,APREV,CPREV/0,0,0,0/	I	9
	IF (LOGS) GO TO 2	I	10
	LAY = .FALSE.	I	11
	JS = JS+1	I	12
	IF (J.EQ.I1) JS = I1	I	13
	IF (JS.GE.I1) LAY = .TRUE.	I	14
	LG = .FALSE.	I	15
	IF (JS.LT.I4) LG = .TRUE.	I	16
	APREV(I4) = A	I	17
	CPREV(I4) = C/RR	I	18
	CALL INTPL (APREV,LG,LAY)	I	19
	CALL INTPL (CPREV,LG,LAY)	I	20
	IF (LG.AND. (.NOT.LAY)) GO TO 3	I	21
	A = APREV(I4)	I	22
	C = CPREV(I4)*RD	I	23
1	RETURN	I	24
2	JS = I0	I	25
3	C = C/19/PR	I	26
	GO TO 1	I	27
	END	I	28
C		I	29

C	-----	J	1
C		J	2
C	SUBROUTINE TO FIND THE INTERPOLATED INITIAL VALUES.	J	3
C		J	4
	SUBROUTINE INTPL (Y,LG,LAY)	J	5
	IMPLICIT REAL*8 (A-H,O-Z) , INTEGER*2 (I-N)	J	6
	REAL*8 A(3),Y(4)	J	7
	LOGICAL*1 LG,LAY	J	8
	DATA A/-1.004453413715894D0,-9.955465862841105D-1,	J	9
	#2.331848862C94706D0/,I1,I2,I3,I4/1,2,3,4/	J	10
	IF (LG) GO TO 2	J	11
	YNEW = 6.681511379052979D-1*Y(I1)	J	12
	DO 1 J=I2,I4	J	13
1	YNEW = YNEW+A(J-I1)*Y(J)	J	14
2	DO 3 J=I1,I3	J	15
3	Y(J) = Y(J+I1)	J	16
	IF (LG) GO TO 5	J	17
	Y(I4) = YNEW	J	18
4	RETURN	J	19
5	IF (LAY) Y(I4) = Y(I3)+Y(I3)-Y(I2)	J	20
	GO TO 4	J	21
	END	J	22
C		J	23
C	=====	J	24

The source program has been made
available by the author through the
following organization :

Physical Sciences Program Exchange
Dept. of Physical Sciences
The Polytechnic
Wulfruna Street
Wolverhampton WV1 1LY
England

THE TWO-CENTER ONE-ELECTRON PROBLEM

	INTERNUCL. DIST.	PHI QUANTUM # NUCL. CHARGES	ELECT. ENERGY	TOTAL ENERGY	SEPARATION CONST.
1	0.20000000000000	1 2.00 1.00	-0.125031441376	9.874968558624	5.999404449399
2	0.40000000000000	1 2.00 1.00	-0.125122139774	4.874877961326	5.997614176003
3	0.60000000000000	1 2.00 1.00	-0.125261481970	3.208071051363	5.994519263440
4	0.80000000000000	1 2.00 1.00	-0.125432856940	2.374567143060	5.990404167018
5	1.00000000000000	1 2.00 1.00	-0.125615512038	1.8743844487962	5.98441324449
6	1.20000000000000	1 2.00 1.00	-0.125787142225	1.540879524441	5.978276151707
7	1.40000000000000	1 2.00 1.00	-0.125936667865	1.302644760706	5.970348158797
8	1.60000000000000	1 2.00 1.00	-0.126016555874	1.123983444126	5.96118427756
9	1.80000000000000	1 2.00 1.00	-0.126044298805	0.985066902306	5.950900733781
10	2.00000000000000	1 2.00 1.00	-0.126002366401	0.873997635597	5.939217747711
11	2.20000000000000	1 2.00 1.00	-0.125938308042	0.783702401049	5.926463036310
12	2.40000000000000	1 2.00 1.00	-0.125703475966	0.707629857367	5.912563946822
13	2.60000000000000	1 2.00 1.00	-0.125451759457	0.64379009774	5.897644531213
14	2.80000000000000	1 2.00 1.00	-0.125138770430	0.589146943956	5.881812512541
15	3.00000000000000	1 2.00 1.00	-0.124770961249	0.541895705418	5.864107128377

APPENDIX II

Separation Constants for the
Angular and Radial Σ -states

Table I
Separation Constant for the Angular Eigenfunctions. ($\ell=1$; $m=0$)

p^2	0	1	2	3	4	5	6	7	8	9	10
Q_a											
0.5	2.091	1.524	0.952	0.374	-0.211	-0.807	-1.413	-2.033	-2.668	-3.318	-3.983
1.5	2.478	2.056	1.632	1.201	0.755	0.287	-0.207	-0.731	-1.285	-1.868	-2.479
2.5	2.639	2.312	1.989	1.666	1.336	0.994	0.633	0.245	-0.177	-0.640	-1.147
3.5	2.458	2.166	1.880	1.595	1.312	1.026	0.736	0.440	0.134	-0.184	-0.521
4.5	2.016	1.725	1.436	1.147	0.857	0.566	0.270	-0.029	-0.335	-0.647	-0.965
5.5	1.393	1.089	0.785	0.478	0.169	-0.145	-0.463	-0.787	-1.118	-1.455	-1.799
6.5	0.641	0.320	-0.003	-0.330	-0.662	-0.998	-1.340	-1.689	-2.044	-2.406	-2.775
7.5	-0.208	-0.547	-0.890	-1.237	-1.589	-1.947	-2.311	-2.681	-3.058	-3.442	-3.833
8.5	-1.135	-1.492	-1.853	-2.219	-2.590	-2.968	-3.351	-3.741	-4.137	-4.540	-4.950
9.5	-2.125	-2.499	-2.877	-3.261	-3.650	-4.045	-4.446	-4.853	-5.267	-5.686	-6.113

Table II

Separation Constant for the Radial Eigenfunctions. ($n=1$; $m=0$)

p^2	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0
Q_r										
.0	-1.484	-1.881	-2.202	-2.485	-2.745	-2.988	-3.219	-3.441	-3.654	-3.862
.1	-1.087	-1.533	-1.877	-2.174	-2.444	-2.694	-2.931	-3.157	-3.375	-3.586
.2	-0.658	-1.173	-1.544	-1.858	-2.138	-2.397	-2.640	-2.872	-3.093	-3.308
.3	-0.183	-0.795	-1.201	-1.534	-1.828	-2.096	-2.346	-2.583	-2.810	-3.028
.4	0.361	-0.397	-0.848	-1.204	-1.512	-1.790	-2.048	-2.292	-2.523	-2.746
.5	1.005	0.028	-0.481	-0.865	-1.190	-1.480	-1.747	-1.997	-2.234	-2.461
.6	1.791	0.487	-0.098	-0.516	-0.861	-1.165	-1.442	-1.699	-1.943	-2.175
.7	2.756	0.990	0.305	-0.155	-0.524	-0.844	-1.132	-1.398	-1.648	-1.885
.8	3.992	1.549	0.731	0.218	-0.179	-0.516	-0.817	-1.092	-1.350	-1.593
.9	5.293	2.179	1.186	0.608	0.177	-0.182	-0.496	-0.783	-1.048	-1.298
1.0	6.869	2.892	1.676	1.016	0.544	0.161	-0.170	-0.468	-0.743	-1.000

Table III

Separation Constant for the Radial Eigenfunctions. ($n=2$; $m=0$)

p^2	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0
Q_r										
.0	-4.741	-5.862	-6.706	-7.415	-8.041	-8.609	-9.135	-9.628	-10.094	-10.538
.1	-4.098	-5.320	-6.212	-6.950	-7.598	-8.182	-8.721	-9.224	-9.699	-10.151
.2	-3.426	-4.763	-5.708	-6.479	-7.149	-7.750	-8.303	-8.817	-9.302	-9.761
.3	-2.725	-4.192	-5.194	-6.000	-6.694	-7.314	-7.881	-8.407	-8.901	-9.369
.4	-1.999	-3.605	-4.670	-5.514	-6.234	-6.873	-7.454	-7.993	-8.497	-8.973
.5	-1.261	-3.004	-4.136	-5.020	-5.767	-6.426	-7.024	-7.575	-8.090	-8.575
.6	-0.522	-2.390	-3.592	-4.519	-5.295	-5.975	-6.589	-7.153	-7.679	-8.174
.7	0.213	-1.766	-3.039	-4.009	-4.816	-5.519	-6.150	-6.728	-7.265	-7.770
.8	0.965	-1.137	-2.476	-3.493	-4.331	-5.057	-5.706	-6.299	-6.848	-7.363
.9	1.779	-0.507	-1.907	-2.969	-3.839	-4.590	-5.258	-5.866	-6.428	-6.953
1.0	2.715	0.122	-1.333	-2.439	-3.342	-4.118	-4.805	-5.429	-6.003	-6.540

APPENDIX III

Determinant of a Pentadiagonal Matrix

For a pentadiagonal $N \times N$ matrix the following substitutions are made :

$$\begin{aligned} \alpha_i &= M_{i,i} , \quad \beta_i = M_{i,i+1} , \quad b_i = M_{i+1,i} , \\ \gamma_i &= M_{i,i+2} , \quad c_i = M_{i+2,i} \end{aligned} \quad [3-1]$$

Then elimination of the elements $M_{i+2,i}$ can be achieved by the following algorithm :

$$\begin{aligned} n &= 0 \\ (1) \rightarrow n &= n+1 \\ \sigma &= c_n / b_n \\ c_n &= 0 \\ b_{n+1} &= b_{n+1} - \alpha_{n+1} \sigma \\ \alpha_{n+2} &= \alpha_{n+2} - \beta_{n+1} \sigma \\ \text{if } n &= (N-2) \text{ stop} \\ \beta_{n+2} &= \beta_{n+2} - \gamma_{n+1} \sigma \\ \text{go to } (1) \end{aligned} \quad [3-2]$$

Then we have what could be called an upper Hessenberg band matrix whose determinant is readily expanded.

Incorporating this into the previous algorithm the following would be obtained :

$$\begin{aligned} n &= 0 , \quad D_0 = 1 , \quad D_1 = \alpha_1 , \quad D_2 = \alpha_1 \alpha_2 - \beta_1 b_1 \\ (1) \rightarrow n &= n+1 \\ \sigma &= c_n / b_n \end{aligned}$$


```

cn = 0
bn+1 = bn+1 - αn+1σ
αn+2 = αn+2 - βn+1σ
Dn+2 = αn+2Dn+1 - βn+1bn+1Dn + γnbnbn+1Dn-1
if n = (N-2) stop ; D = Dn+2
βn+2 = βn+2 - γn+1σ
Dn-1 = Dn
Dn = Dn+1
Dn+1 = Dn+2
go to (1)

```

[3-3]

where D is the determinant of $\tilde{M}$.

However the matrix could be brought into triangular form. The determinant of such a matrix is :

$$D = \prod_{i=1}^N \alpha_i \quad [3-4]$$

This is achieved by the following algorithm :

```

n=0 , D=α1
(1)  n=n+1
      if n=(N-1) go to (2)
      σ1 = cn/bn
      cn = 0
      bn+1 = bn+1 - σ1αn+1
      αn+2 = αn+2 - σ1βn+1
      βn+2 = βn+2 - σ1γn+1
(2)  σ2 = bn/αn
      bn = 0
      αn+1 = αn+1 - σ2βn
      βn+1 = βn+1 - σ2γn
      D = αn+1D
      if n ≤ (N-1) go to (1)
      stop

```

[3-5]

This algorithm requires essentially 8N multiplications

whereas the previous algorithm required $10N$ multiplications to evaluate the determinant.

Both algorithms were coded in Fortran IV as shown below but no extensive comparison of their performance was made.

The arrays in the subroutines contain the following :

$$\begin{aligned} C(i) &= c_i, \quad B(i) = b_i, \quad AL(i) = \alpha_i, \\ BE(i) &= \beta_i, \quad GA(i) = \gamma_i \end{aligned} \quad [3-6]$$

and $NM1 = N-1$, $NM2 = N-2$.

The subroutines shown are for complex algorithms and actually evaluate the norm of the determinant.


```

REAL FUNCTION PENT*8 (C,B,AL,BE,GA,NM2)
IMPLICIT COMPLEX*16 (A-H,O-Z)
COMPLEX*16 C(2),B(2),AL(2),BE(2),GA(2)
REAL*8 CDABS
DATA I1/1/
J=0
DM2=(1.0D0,0.0D0)
DM1=AL(I1)
D=AL(I1)*AL(2)-B(I1)*BE(I1)
1 J=J+I1
J1=J+I1
J2=J1+I1
SIGMA=C(J)/B(J)
B(J1)=B(J1)-AL(J1)*SIGMA
AL(J2)=AL(J2)-BE(J1)*SIGMA
P5=D*AL(J2)-DM1*B(J1)*BE(J1)+DM2*GA(J)*B(J)*B(J1)
IF (J.EQ.NM2) GO TO 2
BE(J2)=BE(J2)-GA(J1)*SIGMA
DM2=DM1
DM1=D
D=P5
GO TO 1
2 PENT=CDABS(P5)
RETURN
END

```

```

REAL FUNCTION PENT*8 (C,B,AL,BE,GA,NM1)
IMPLICIT COMPLEX*16 (A-H,O-Z)
COMPLEX*16 C(2),B(2),AL(2),BE(2),GA(2)
REAL*8 CDABS
LOGICAL*1 L1
DATA I1/1/
L1=.TRUE.
N=0
P5=AL(I1)
1 N=N+I1
IF (N.EQ.NM1) L1=.FALSE.
N1=N+I1
IF (.NOT.L1) GO TO 2
N2=N1+I1
SIGMA=C(N)/B(N)
B(N1)=B(N1)-SIGMA*AL(N1)
AL(N2)=AL(N2)-SIGMA*BE(N1)
BE(N2)=BE(N2)-SIGMA*GA(N1)
2 SIGMA=B(N)/AL(N)
AL(N1)=AL(N1)-SIGMA*BE(N)
BE(N1)=BE(N1)-SIGMA*GA(N)
P5=P5*AL(N1)
IF (L1) GO TO 1
PENT=CDABS(P5)
RETURN
END

```


"The only true wisdom", the caribou wizard told the explorer Rasmussen, "lives far from mankind, out in the great loneliness, and it can be reached only through suffering. Privation and suffering alone can open the mind of man to all that is hidden to others".

H. Osterman, Report of the
Fifth Thule
Expedition
1921-24

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